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# *Leonard James Spencer, Editor 1900–55: An appreciation.*

By A Past President

DR. SPENCER was appointed Editor of the 'Mineralogical Magazine' in late 1900 and retired from the office in December 1955. It is my privilege now to thank Dr. Spencer on behalf of the Mineralogical Society for his superlative performance of duties willingly and joyfully borne throughout these fifty-five years.

Mr. Spencer was elected to the Society on 6th February, 1894. His impact on the Journal was immediate: the number (48) issued in September of that year contained 10½ pages of abstracts by L. J. S., occupying fully one-eighth of the publication. This number was the final one to complete Volume X: what a golden opportunity for young Spencer: he seized it with both hands and presented to the Editor an 'Index of Authors and Subjects, Volumes I–X' with, for good measure, a 'Supplementary List of Errata, vols. I–X' running to five pages of print! The preparation of the Index, which extends to 88 pages of closely printed matter', says the Report of Council for Session 1895–6, 'was undertaken as a labour of love by Mr. L. J. Spencer to whom the hearty thanks of the Society are due.'

Thereafter research papers and abstracts came from his pen in a steady stream. In 1897 he contributed his first 'List of new mineral names' supplementary to which a list was destined to appear triennially as the final paper of each volume. At the Annual Meeting on 14th November 1899 Spencer was elected to the Council, which since then has never been without his counsel and services, for, on the retirement of H. A. Miers from the Editorship on the completion of Volume XII by Number 58, November 1900, the Council was 'glad to report that Mr. Spencer is

willing to undertake the duties and has been appointed Editor'. Editor he has remained to see the completion of Volume XXX by Number 231 issued in December 1955.

In the course of his long term of duty Spencer has edited 901 original papers, of which he himself has provided 49 and contributed to five others in addition to his Lists of new mineral names, for publication in the Magazine. Responsibly, and joyously one imagines, as he set about his duties in 1901 when the number printed that year totalled 114 pages, he could not have foreseen that the annual printing would rise to over 500 pages. But so intense was, and remains, his interest in the science and its advancement and so deep his love for the Magazine that a foresight of the future could have brought naught but happy incentive. Wide-ranging knowledge of his science and pride in the prestige of his Journal were the foundations of the excellence of his Editorship. Tirelessly and relentlessly in the interests of the Society and the Journal he has disciplined authors, publishers, and himself. Though, with Pope, he might have said

> . . . I read
> With honest anguish, and an aching head;
> And drop at last, but in unwilling ears,
> This saving counsel, 'Keep your piece nine years',

his own words[1] are these: 'I have had no hesitation in inviting [his word] authors to reconsider their papers and if necessary to rewrite and curtail them.' He continues: 'I have with very few exceptions found authors most reasonable and grateful for assistance.' Small wonder he found them so for his knowledge was profound and his purpose selfless! Retaining proofs for a minimum of time and tolerating no tardiness by the authors, he has harried the publishers as well so that each number should appear duly on the day appointed. In the difficult times after 1945 of paper and labour shortages and of confused transition to peacetime activities his anxieties and labours in achieving prompt publication of each number were prodigious. Furious as delays of a week to a fortnight made him, he fortunately rarely had to endure the pain and self-condemnation which the non-appearance of a number within the month for which he had press-marked it would assuredly have caused.

Among his anxieties as Editor Spencer has always had that of costs. Thanks to his meticulous editing additional costs arising from corrections to proofs have always been extremely low. Constantly rising

[1] Amer. Min., 1941, vol. 26, p. 165.

prices have harassed him, especially in recent years: but this problem is an old one. His solution in 1920 illustrates both his financial acumen and his willingness to undertake still more work for the benefit of the Society and its Journal: 'The Editor reported that owing to the increased cost of printing he was issuing smaller numbers of the Journal at more frequent intervals, the price for each number remaining as before. . . .' (Proc. Min. Soc., vol. 19, 1921, p. xxiv). This solution introduced the quarterly issue of Magazine and Abstracts which now rules.

In the early numbers of the 'Mineralogical Magazine' reviews of books and abstracts of important papers that had appeared in other journals were a constant feature. From his first year as a member of the Society Spencer was, as we have seen, an enthusiastic contributor of abstracts. As work in mineralogical and in other branches of science increased in volume and appeared in new journals and more various languages, abstracts grew ever more essential to research. The 'International Catalogue of Scientific Literature' having been instituted to meet this need, the publication of mineralogical abstracts in the Magazine was suspended, and from 1900 to 1914 Spencer contributed his abstracts on mineralogy to the 'Catalogue'. This period came to an end in 1914. The question of resuming publication of abstracts in the Magazine was considered by the Council in 1917, but not until 1920 was the decision taken to publish abstracts once more. How eagerly and impatiently must the Editor have awaited the authority to go ahead! With the first number of the Magazine issued after this decision, vol. 19, no. 88, 1920, there appeared vol. 1, no. 1 of 'Mineralogical Abstracts' comprising 37 items on 16 pages, all by L. J. S. It was bound in with the Magazine, as now, as a separately paged appendix, but could be bought separately. When the first volume was completed in 1922 its abstracts totalled 424 pages of which Spencer had contributed 262, and it included the first of those remarkable indexes, arranged by topography and by subject, which have proved a boon to workers in mineralogical and kindred sciences. In the thirty-six years covered by the twelve volumes of 'Mineralogical Abstracts' which have now been published, Spencer's own contribution of text is of the order of 5000 pages. As Editor he has checked all references, in a multiplicity of languages and scripts, contained in the 7322 pages. Examination of the 'lists of errata', which with a driving passion for accuracy he has included with each subsequent index number, provides one measure of his editorial efficiency; errors of reference are no more than 0·002 %: no doubt he would say that the figure is still higher than it ought to be.

The time that Spencer has saved and the help that he has given crystallographers, mineralogists, and petrologists by his abstracts and by the rich, systematic, and accurate indexes which close each volume are incalculable. 'It is a mere statement of fact', said Professor A. N. Winchell in presenting to Dr. Spencer in 1940 the Roebling Gold Medal of the Mineralogical Society of America, 'to say that Mineralogical Abstracts has come to be recognised very generally as the best publication of its kind. It is now the chief source of prompt information regarding all publications in the field of mineralogy, and, as such, it is of fundamental importance in all research work in our science.' In his reply Spencer said 'the indexing has been taken seriously'.

It must suffice only to mention his twenty 'Lists of new mineral names' and 'Biographical notices of mineralogists recently deceased'. 'Lists' for Spencer is a wide term: his lists include full reference to the original paper, etymology of the name, concise chemical and crystallographic information on the mineral, reference to comparable species or variety, and finally a page and volume reference to the Abstracts. Occasionally he relieves his labour with a 'crack': 'Poly-, prefix in some 30 mineral names. . . . It has now been extended with other significations, giving rise to polyonymous complexities.'[1] In the series of Biographical notices begun in 1921 he has paid homage to 375 workers in his science, and has periodically indicated to surviving colleagues their prospects of mortality.

Not quite so spry physically as he used to be, Spencer continues alert and blithe in spirit. 'I have had a good innings with the Min. Mag.', he writes in a letter of 5th December of this year, 'for which I started writing abstracts and notes in 1894. I am glad to be now free to get on with my own work. I have ideas for several books. . . .' May he have many happy years developing and setting forth these ideas, and editing and indexing their printed formulation to the further benefit of mineralogical science and, above all, to his own satisfaction.

J. P.

*14th December, 1955.*

[1] Min. Mag., 1955, vol. 30, p. 743.

# *Okenite and nekoite (a new mineral).*

(With Plate I.)

By J. A. Gard, B.Sc., and H. F. W. Taylor, B.Sc., Ph.D.

Department of Chemistry, University of Aberdeen.

[Read 9 June, 1955.]

*Summary.*—The unit cell of okenite ($CaO.2SiO_2.2H_2O$) has been determined for a specimen from Bombay, India, using a combination of X-ray, electron-microscope, and electron-diffraction methods. It is anorthic with[1] $a$ 9·84, $b$ 7·20, $c$ 21·33 Å., $\alpha$ 90·0°, $\beta$ 103·9°, $\gamma$ 111·5°, elongation $b$, Z = 9. These data are compatible with the goniometric results of Bøggild (1922) and allow the latter to be interpreted.

A specimen from Crestmore, California, which Eakle (1917) had described as okenite, was also examined. It was found to be a new species, having the same composition as okenite but distinguishable from it by its optical properties, X-ray powder data, and unit cell. The latter is anorthic with[1] $a$ 7·60, $b$ 7·32, $c$ 9·86 Å., $\alpha$ 111° 48′, $\beta$ 86° 12′, $\gamma$ 103° 54′, elongation $b$, Z = 3. Because of the relation to okenite, the name *nekoite* is suggested.

## Part I. Okenite.

OKENITE ($CaO.2SiO_2.2H_2O$) was discovered on Disko Island, Greenland. It was first analysed by von Kobell[2] and described by Breithaupt.[3] It has since been found in other localities, usually associated with basalt. Satisfactory optical and goniometric data were first obtained by Bøggild;[4] the former are given in table I and the latter in table IV. These data showed that okenite was anorthic, but the axial ratios could not be obtained. The optical data were confirmed by Tilley and Alderman.[5] X-ray powder data have been reported (table II), and X-ray photographs of fibrous aggregates have shown that okenite belongs to the group of fibrous hydrated calcium silicates having a repeat distance of about 7·3 Å. in the fibre direction.[6] No single-crystal data have been reported and the unit cell has not previously been determined.

[1] This cell is not in conventional orientation: see pp. 13 and 16, footnotes.

[2] F. von Kobell, Arch. gesammte Naturlehre (Kastner), 1828, vol. 14, p. 333.

[3] A. Breithaupt, Ann. Phys. Chem. (Poggendorff), 1845, vol. 64, p. 170.

[4] O. B. Bøggild, Kgl. Danske Vidensk. Selsk., Math.-fys. Medd., 1922, vol. 4, no. 8 [M.A. 2–59].

[5] C. E. Tilley and A. R. Alderman, Min. Mag., 1934, vol. 23, p. 513.

[6] H. F. W. Taylor, Proc. Int. Symp. Reactivity of Solids, Gothenburg, 1952 p. 677.

*Optical and X-ray investigation.*

A specimen from the Syhadree Mountains, Bombay, India (B.M. 27989), was employed. It consisted of fibrous aggregates showing parallel extinction, positive elongation, low birefringence, and mean

TABLE I. Optical and unit-cell data for okenite and nekoite.

| *Optical data.* | Okenite. | Nekoite. |
|---|---|---|
| Locality: | Disko Island and Faeroe Islands | Crestmore, California |
| Investigator: | Bøggild | This investigation |
| Habit: | Usually fibrous. Single crystals are prisms with one good cleavage | Needles with one good cleavage |
| Twinning: | On the cleavage face, very common. On the prism axis, rare | Needles show repeated twinning with lamellae parallel to the cleavage |
| Indices: | $\alpha'$ 1·530, $\gamma'$ 1·541 | Mean 1·535±0·002 (Na) |
| Birefringence: | 0·011 | Very low |
| Extinction: | Crystals lying on the cleavage have parallel extinction, + elongation. In other orientations, extinction is oblique; for laths lying on edge it makes 32±2°, and for laths standing on end, 25° with the cleavage trace | Always inclined. Individual lamellae lying on the cleavage have − elongation, extinction angle 26°. Lamellae standing on edge have − elongation, extinction of adjacent twin lamellae symmetrical at 5° to the twin boundaries |
| Interference figure: | ? | Individual lamellae lying on the cleavage give a poor biaxial + acute bisectrix figure |
| 2V: | Probably large | 70° approx. |
| Optic sign: | Negative* | Positive |
| Optic orientation: | ? | $X$ makes about 26° with the needle axis, and $Z$ is roughly perpendicular to the cleavage |
| *Unit-cell data.* | | |
| System: | Anorthic | Anorthic |
| Parameters: | $a$ 9·84 Å. | $c$ 9·86 Å. |
| | $b$ 7·20 | $b$ 7·32 |
| | $c$ 21·33 (3×7·11) | $a$ 7·60 |
| | $\alpha$ 90° | $\gamma$ 103° 54′ |
| | $\beta$ 103·9° | $\beta$ 86° 12′ |
| | $\gamma$ 111·5° | $\alpha$ 111° 48′ |
| Cell contents: | 9[CaO.2SiO$_2$.2H$_2$O] | 3 [CaO.2SiO$_2$.2H$_2$O] |
| Fibre direction: | $b$ | $b$ |
| Cleavage: | (001) | (100) |

* C. E. Tilley and A. R. Alderman, loc. cit., for a specimen from Scawt Hill (Northern Ireland).

refractive index, 1·540±0·003. Similar data were obtained by Christie[1] for a specimen of a comparable degree of crystallinity, also from Bombay. The data are compatible with those obtained by Bøggild for single crystals from the type locality and elsewhere although, because they relate to fibrous aggregates, they are necessarily less detailed.

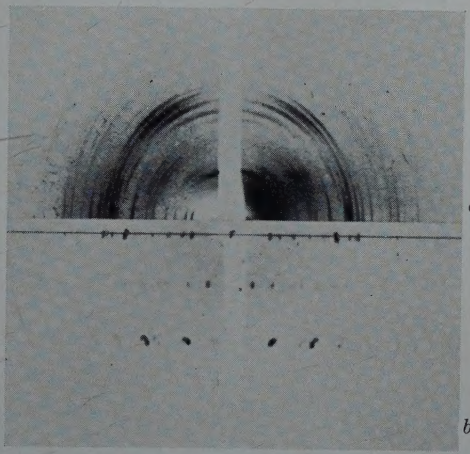


FIG. 1. X-ray rotation photographs about the needle or fibre axis. Cu-$K\alpha$ radiation. *a*, okenite, Bombay; *b*, nekoite, Crestmore.

X-ray powder data, obtained using 6-cm. and 19-cm. diameter cameras with Cu-$K\alpha$ radiation, are included in table II. They are in substantial agreement with the various sets of data obtained by previous workers, including those of McMurdie and Flint, which probably relate to material from the type locality. Minor differences exist between all the sets of data, but they can probably be attributed to the presence of impurities in some or all of the specimens, and the data indicate that all consist of substantially the same mineral.

The X-ray fibre rotation patterns previously reported, and reproduced in fig. 1*a*, showed that the repeat distance along the fibre axis (later shown to be *b*) was 7·20 Å. They also enabled the *k*-indices of the powder reflections to be determined, and these indices are also included in table II.

Attempts to isolate single crystals of sufficient size for X-ray work were unsuccessful, even the thinnest fibres giving rotation photographs. Complete indexing of the data by X-ray means was therefore not possible, and electron diffraction was employed.

[1] W. A. K. Christie, Rec. Geol. Survey India, 1925, vol. 56, p. 199 [M.A. 3–287].

TABLE II. X-ray powder data for okenite and nekoite. Spacings in Å.

| 1. | | 2. | | | 3. | | 4. | | 5. | |
|---|---|---|---|---|---|---|---|---|---|---|
| *d.* | *I.* | *d.* | *I.* | *k.* | *hkl.* | *d.* | *d.* | *I.* | *hkl.* | *d.* |
| | | 21 | vvs | 0 | 001 | 20·6 | | | | |
| 10·61 | 30 | 10·3 | vw | 0 | 002 | 10·3 | | | | |
| 8·87 | 100 | 8·8 | vs | 0 | 200 | 8·84 | 9·25 | vs | 001 | 9·15 |
| 7·65 | 70 | 7·4 | mw | 0 | 201 | 7·46 | 7·45 | w | 100 | 7·39 |
| 6·72 | 70 | 6·8 | vw | 1 | 110 | 6·67 | 6·61 | w | $01\bar{1}$ | 6·63 |
| | | 6·19 | w | 0 | $20\bar{3}$ | 6·26 | | | 010 | 6·61 |
| 5·72 | 30 | 5·79 | vvw | 1 | $11\bar{2}$ | 5·86 | | | $(10\bar{1}$ | 5·82) |
| | | | | | | | 5·64 | w(b) | 101 | 5·67 |
| 5·35 | 10 | 5·22 | w | 0 | 004 | 5·25 | | | $\bar{1}1\bar{1}$ | 5·55 |
| | | | | | | | 4·55 | vw | 002 | 4·57 |
| 4·57 | 90 | 4·42 | w | 0 | 400 | 4·42 | | | (110 | 4·44) |
| 4·23 | 70 | 4·27 | vvw(b) | 1 | 311 | 4·28 | | | | |
| 4·08 | 70 | 4·08 | vw | 0 | 401 | 4·11 | 4·14 | vw | $\bar{1}1\bar{2}$ | 4·20 |
| 3·90 | 70 | 3·90 | vw | 1 | 114 | 3·90 | | | | |
| 3·56 | 90 | 3·56 | vs | 0 & | 405 | 3·56 | | | | |
| | | | | 2 | 021 | 3·55 | | | | |
| 3·35 | 60 | 3·34 | vvw | 2 | $22\bar{1}$ | 3·34 | 3·36 | vs(b) | 201 | 3·39 |
| | | | | | 220 | 3·33 | | | 020 | 3·30 |
| | | | | | 510 | 3·18 | | | | |
| | | 3·22 | vvw | 1 | $51\bar{3}$ | 3·18 | | | | |
| | | | | | 116 | 3·18 | | | | |
| | | | | | $60\bar{2}$ | 3·05 | | | | |
| | | 3·07 | s | 0 & | $20\bar{7}$ | 3·04 | | | | |
| 3·09 | 90 | | | 2 | 222 | 3·08 | 3·04 | w | 003 | 3·05 |
| | | 3·05 | s | 0 | $60\bar{1}$ | 3·03 | | | | |
| | | | | | $60\bar{3}$ | 3·00 | | | | |
| | | | | | 404 | 2·99 | | | | |
| (2·99 m)* | | 2·98 | ms | 0 & | $22\bar{4}$ | 3·01 | | | | |
| | | | | 2 | 024 | 2·95 | | | | |
| | | | | | 600 | 2·95 | | | | |
| | | | | | 206 | 2·95 | | | $12\bar{1}$ | 2·94 |
| 2·92 | 90 | 2·93 | vs | 0 & | 007 | 2·94 | 2·92 | w | $20\bar{2}$ | 2·91 |
| | | | | 2 | 223 | 2·89 | | | 202 | 2·84 |
| | | 2·80 | w | 0 | $40\bar{7}$ | 2·81 | | | $12\bar{2}$ | 2·81 |
| 2·78 | 70 | 2·77 | ms | 2 | 420 | 2·79 | 2·82 | vs | $(02\bar{3}$ | 2·81) |
| 2·69 | 30 | 2·68 | vw | 0 | 602 | 2·66 | | | 103 | 2·79 |
| 2·53 | 40 | 2·53 | w | 0 | $40\bar{8}$ | 2·53 | | | 120 | 2·78 |
| | | 2·44 | vvw | 2 | 423 | 2·45 | 2·47 | ms | 121 | 2·45 |
| 2·39 | 60 | 2·38 | vw | 0 | $20\bar{9}$ | 2·37 | 2·36 | vw | 301 | 2·36 |
| | | | | | $22\bar{7}$ | 2·32 | | | | |
| | | | | | $62\bar{1}$ | 2·32 | 2·28 | vw | | |
| 2·30 | 40 | 2·30 | vw | 2 | 424 | 2·30 | | | | |
| | | | | | 226 | 2·28 | | | | |
| | | | | | $60\bar{8}$ | 2·25 | | | | |
| 2·22 | 40 | 2·24 | w | 0 | 407 | 2·24 | | | | |
| | | 2·20 | w | 2 | $42\bar{7}$ | 2·21 | 2·20 | w | | |
| (2·16 w)* | | 2·15 | mw | 0 | 605 | 2·15 | 2·15 | vvw | | |
| | | | | | 209 | 2·15 | | | | |
| 1·98 | 60 | 1·98 | vw | 0 | 803 | 1·96 | 2·09 | vvw | | |
| | | 1·91 | vw(b) | 0 | 0.11.0 | 1·87 | | | | |
| | | | | | $62\bar{8}$ | 1·91 | | | | |
| 1·88 | 60 | 1·89 | w | 2 | 820 | 1·88 | 1·90 | mw | | |
| | | | | | 427 | 1·88 | | | | |
| | | 1·84 | vw | 2 | 625 | 1·84 | | | | |
| | | | | | 821 | 1·82 | | | | |

TABLE II (*cont.*)

| 1. | | 2. | | | 3. | | 4. | | 5. | |
|---|---|---|---|---|---|---|---|---|---|---|
| *d.* | *I.* | *d.* | *I.* | *k.* | *hkl.* | *d.* | *d.* | *I.* | *hkl.* | *d.* |
| 1·80 | 90 | 1·80 | s | 4 | 040 | 1·80 | 1·83 | ms | | |
| 1·77 | 30 | 1·77 | vw | | | | 1·79 | mw | | |
| 1·73 | 20 | 1·74 | vvw | | | | | | | |
| | | 1·71 | vvw | | | | | | | |
| 1·68 | 30 | 1·68 | vvw | | | | 1·69 | w | | |
| 1·63 | 10 | 1·64 | vvw(b) | | | | 1·65 | vw | | |
| | | | | | | | 1·615 | vw | | |
| 1·58 | 40 | 1·59 | ms | | | | 1·583 | vvw | | |
| 1·55 | 30 | 1·56 | mw | | | | 1·546 | w | | |
| 1·51 | 40 | 1·52 | mw | | | | | | | |
| 1·45 | 40 | 1·47 | vvw | | | | 1·455 | vw | | |
| 1·43 | 30 | 1·45 | mw | | | | 1·413 | vvw | | |
| 1·39 | 30 | 1·39 | vvw | | | | 1·392 | vvw | | |
| 1·36 | 40 | 1·36 | mw | | | | 1·357 | vw | | |
| 1·33 | 40 | 1·33 | w | | | | | | | |
| 1·28 | 20 | 1·289 | w | | | | | | | |
| 1·26 | 20 | 1·256 | w | | | | | | | |
| 1·21 | 30 | 1·207 | w | | | | | | | |
| 1·19 | 30 | 1·193 | vw | | | | | | | |
| 1·14 | 10 | 1·146 | vw | | | | | | | |
| 1·11 | 10 | 1·112 | w | | | | | | | |
| | | 1·080 | w | | | | | | | |
| | | 1·064 | w | | | | | | | |

1. Okenite, Bordö, Faeroe Islands. American Society for Testing Materials. Card File of X-Ray Diffraction Data. Cards Nos. 2–0069 and 2–0070, from data supplied by Imperial Chemical Industries Ltd., Northwich, England. Relative intensities on numerical system.†
2. Okenite, B.M. 27989, Syhadree Mtns., Bombay. This investigation. Cu-$K\alpha$ radiation. $k$-indices deduced from fibre photographs.
3. Okenite. Indices and spacings calculated on the basis of the monoclinic pseudocell of the present investigation.
4. Nekoite, U.S.N.M. 95637, Crestmore, California. This investigation. Cu-$K\alpha$ radiation.
5. Nekoite. Anorthic indices and calculated spacings. Indices and calculated spacings of weak reflections making minor contributions to the powder photograph are enclosed in parentheses; those of very weak reflections making negligible contributions are omitted.

* Data of McMurdie and Flint (see below); these lines were not recorded in the I.C.I. data.

† Less complete powder data for okenite were given by L. M. Clark and C. W. Bunn (Journ. Soc. Chem. Ind., 1940, vol. 59, p. 155 [M.A. 8–116]), locality and radiation not stated; and by H. F. McMurdie and E. P. Flint (Journ. Res. Nat. Bur. Stand. U.S.A., 1943, vol. 31, p. 225 [M.A. 9–45]; A.S.T.M. Index, Card No. 2–0068), Disko Island, Greenland, Cu-$K\alpha$ radiation.

## *Electron-diffraction investigation.*

A Metropolitan-Vickers EM3 electron microscope was used. The operation of this type of instrument has been described elsewhere.[1] It

[1] C. E. Challice, Proc. Physical Soc., ser. B, 1950, vol. 63, p. 59; J. F. Brown and D. Clark, Acta Cryst., 1952, vol. 5, p. 615; T. B. Rymer, Brit. Journ. Appl. Phys., 1953, vol. 4, p. 297.

can be used both as an electron microscope and as a diffraction instrument. In the latter case, the area of the specimen from which the diffraction pattern is obtained can be reduced to a circle about $2\mu$ in diameter. A pattern can thus be obtained from a very small individual crystal, and its orientation relative to the outline of the crystal can be determined. The diffraction pattern is a practically undistorted picture of the reciprocal lattice in the plane through the origin and normal to the electron beam.

Specimens were prepared by crushing a little material in water and allowing a drop of the dilute suspension to dry on a film-coated specimen grid. An electron micrograph is shown in pl. I, A, B, and C. The crystals were laths of average dimensions $6\times2\times0{\cdot}5$ $\mu$. On closer examination these were seen to consist of very thin parallel sheets, with excellent cleavage in planes parallel to the supporting film, i.e. normal to the electron beam. Individual sheets were found by shadow-casting[1] to vary in thickness between about 20 and 250 Å. It will be shown later that these sheets are possibly twin lamellae.

The laths had well-defined edges along a direction later identified with the fibre axis of the X-ray rotation photograph, but no faces other than the one cleavage face could be distinguished.

The crystals all gave substantially identical diffraction patterns, a typical example being shown in fig. 2*a*. If the cleavage plane normal to the beam is taken as (001), two unit-cell dimensions $a$ and $b$, and the angle $\gamma$, can be obtained directly from the pattern. The reciprocal lattice direction $c^*$ coincides with the electron beam, but the $(0a^*b^*)$ plane coincides with (001) only if $\alpha$ and $\beta$ are both 90°. Evidence will be presented to show that this is not the case, and that the pattern is therefore a projection of the $(0a^*b^*)$ plane in the direction of the beam, the large number of reflections recorded being due to the fact that the reciprocal lattice points are elongated parallel to the thin direction of the crystal.

Measurement of the pattern showed that all the reflections could be fitted geometrically on to a $c$-face centred monoclinic reciprocal lattice, and the resulting dimensions for the real and reciprocal cells are given in fig. 3*a*. The relative intensities depend on too many factors to confirm or disprove monoclinic symmetry, but the goniometry and optical data strongly indicate anorthic symmetry. It therefore seemed preferable to express the results in terms of an anorthic unit cell. These are given for the real and reciprocal cells in fig. 3*b*.

[1] R. E. Williams and R. W. G. Wyckoff, Journ. Appl. Phys., 1944, vol. 15, p. 712.

The other three parameters, $c$, $\alpha$, and $\beta$, were obtained from a comparison of electron-diffraction and X-ray data. The two longest X-ray spacings (21 and 10·3 Å.; table II) have ($h0l$) indices, but are too large to correspond to any of the ($h00$) reflections, found using electron diffraction. They therefore have ($00l$) indices, and were assumed to be respectively (001) and (002), giving $c^* = 1/(20{\cdot}6)$ Å.$^{-1}$

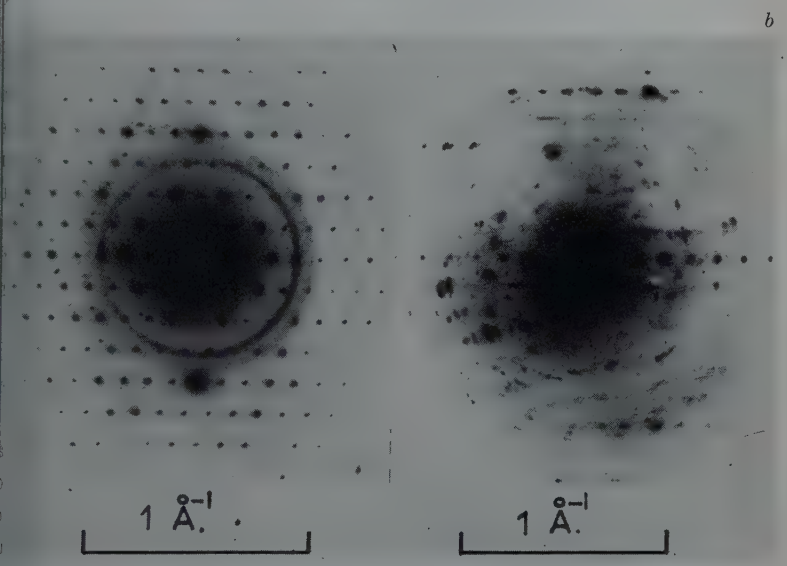


FIG. 2. Electron-diffraction patterns given by single flakes in the electron microscope. *a*, okenite lying on (001); *b*, the same after heating at 1000° C. Fibre direction vertical in each case.

The repeat distance of 7·20 Å. along the fibre direction, found using X-rays, agrees with the value of $b$ obtained with electron diffraction. The ($0a^*b^*$) plane of the reciprocal lattice therefore coincides with (001) along the fibre direction ($b$), making $\alpha = 90°$.

The third longest X-ray spacing, of approximately 8·8 Å., also has ($h0l$) indices. It was assumed that that of 4·42 Å. was its second order, giving a more precise value of 8·84 Å. This does not agree with any of the apparent ($h00$) spacings measured by electron diffraction, but is near enough to the apparent (100) (monoclinic (200)) spacing of 9·09 Å. (fig. 3) to suggest that the two are probably associated with the same elongated reciprocal lattice point. If this assumption is correct, the angle ($90 - \beta^*$) which $a^*$ makes with (001) is equal to $\cos^{-1}$ (8·84/9·09),

or approximately 13° (fig. 4). $\beta$ is therefore approximately (90+13)°, or 103°.

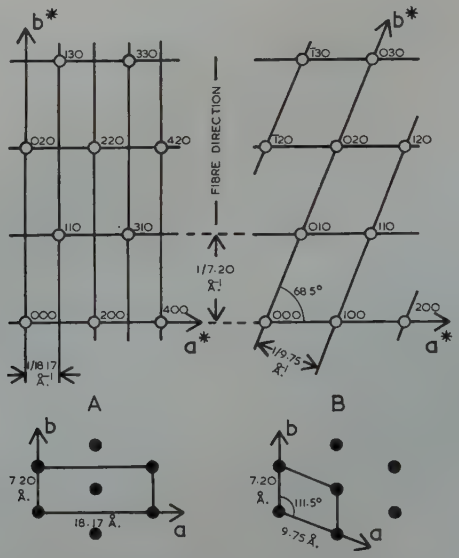


FIG. 3. Interpretation of the electron-diffraction pattern of okenite. A (*left*): observed reflections indexed on the (001) projection of a geometrically monoclinic *c*-face centred reciprocal lattice, with the corresponding real pseudo-cell below. B (*right*): the same reflections indexed on the (001) projection of an anorthic reciprocal lattice, with the corresponding real unit cell below.

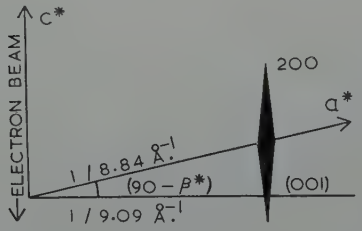


FIG. 4. Determination of the approximate value of pseudo-monoclinic $(90-\beta^*)$ for okenite, by comparison of X-ray and electron-diffraction data. Section of the reciprocal lattice passing through the origin and normal to *b*, showing how the apparent *a*-axis of 9·09 Å. derived from electron-diffraction data may be reconciled with the value of 8·84 Å. given by the X-ray data.

*Unit cell, twinning, and goniometric data.*

From the above considerations the monoclinic pseudo-cell was assumed provisionally to have the parameters $a$ 18·18, $b$ 7·20, $c$ 21·2 Å., $\beta$ 103°. In order to check that these parameters were basically correct, and also to obtain a more accurate value of $\beta$, spacings were calculated and compared with the X-ray powder and fibre data. Several values of $\beta$ were tried, and good agreement between observed and calculated values, as regards both spacings and $k$-indices, was obtained for $\beta = 105°$ (table II). The revised parameters for the monoclinic pseudo-cell were thus found to be[1] $a$ 18·30, $b$ 7·20, $c$ 21·33 Å., $\beta$ 105°. The corresponding anorthic unit cell has[2] $a$ 9·84, $b$ 7·20, $c$ 21·33 Å., $\alpha$ 90·0°, $\beta$ 103·9°, $\gamma$ 111·5°.

In the course of the electron-diffraction investigation, attempts were made to determine $c$ directly by the method of Laue zones.[3] These were unsuccessful, no division of the pattern into zones being observed, even though the specimen stage was tilted at angles up to 35° from the normal position, and diffraction patterns recorded for many crystals with their fibre axes approximately parallel to the axis of tilt. This remarkable absence of zoning is accounted for if the crystals have repeated lamellar twinning across the cleavage plane, so that the continuous row of lattice points along $c$, needed for the production of Laue zones, is not present. Twinning according to this law was found by Bøggild to be very common in larger crystals. The present results, including the appearance of the crystals in the electron microscope (pl. I), suggest that repeated twinning of this type may occur in the fibrous material from Bombay on a very small scale in which individual twin lamellae are perhaps sometimes only a few unit cells thick. This might be expected to have some influence on the X-ray pattern; in fact, Heller[4] observed minor variations in the patterns obtained from different fibres taken from this same specimen of okenite, and mentioned complex twinning as one possible explanation.

Calculation from the unit-cell data obtained in the present investiga-

[1] This cell, having $c > a$, is not in the conventional orientation. Application of the transformation matrix $\|001/0\bar{1}0/100\|$ gives: $a$ 21·33, $b$ 7·20, $c$ 18·30 Å., $\beta$ 105°; fibres parallel to $b$, cleavage (100).

[2] This cell is not in the conventional orientation. Application of the transformation matrix $\|100/00\bar{1}/010\|$ gives: $a$ 9·84, $b$ 21·33, $c$ 7·20 Å., $\alpha$ 90·0°, $\beta$ 111·5°, $\gamma$ 86·1°; fibres parallel to $c$, cleavage (010).

[3] J. F. Brown and D. Clark, loc. cit.

[4] L. Heller, Proc. Third Internat. Symposium Chemistry of Cement, London, 1952; Cement and Concrete Association, London, 1954, p. 237.

tion and the chemical analysis and specific gravity (2·302) determined by Christie, gave the cell contents listed in table III. They indicate the ideal formula $9[CaO.2SiO_2.2H_2O]$ or $Ca_9Si_{18}O_{63}H_{36}$ per (anorthic) unit cell.

Bøggild obtained approximate goniometric data for very small single crystals from Disko Island and the Faeroe Isles. He described them as laths with cleavage (010) and length *c*. His results, obtained using a

TABLE III. Chemical analyses and unit-cell contents of okenite and nekoite.

| | 1. | 2. | | 1a. | 2a. |
|---|---|---|---|---|---|
| $SiO_2$ ... ... ... | 53·88 | 56·17 | Si ... | 16·86 | 6·21 |
| $Al_2O_3$ ... ... ... | 0·08 | — | Al ... | 0·04 | — |
| $Fe_2O_3$ ... ... ... | 0·01 | — | Fe ... | — | — |
| CaO ... ... ... | 27·61 | 26·10 | Ca ... | 9·00 | 3·09 |
| SrO ... ... ... | 0·27 | — | Sr ... | 0·04 | — |
| $Na_2O$ ... ... ... | 0·12 | — | Na ... | 0·06 | — |
| $K_2O$ ... ... ... | 0·06 | — | K ... | 0·02 | — |
| $H_2O$ ... ... ... | 18·02 | 16·83 | H ... | 37·8 | 12·4 |
| | 100·05 | 99·10 | O ... | 61·6 | 21·7 |
| Sp. gr. ... ... ... | 2·302 | 2·206 | | | |

1. Okenite, Bombay. W. A. K. Christie (analysis no. 2).
2. Nekoite, Crestmore. A. S. Eakle (analyst, W. F. Foshag).
1a. Atomic cell-contents calculated from analysis 1 (anorthic cell).
2a. Atomic cell-contents calculated from analysis 2 (anorthic cell).

two-circle goniometer, are given in table IV, which shows also that each of the faces which he measured can be satisfactorily explained on the basis of the anorthic cell found in the present investigation. Bøggild's choice of axes was not retained, because it obscures the relation between

TABLE IV. Comparison of observed and calculated goniometric data for okenite.

| Indices. | | Bøggild. | | Calculated. | |
|---|---|---|---|---|---|
| Bøggild. | New (anorthic). | $\phi$. | $\rho$. | $\phi$. | $\rho$. |
| (010) | (001) | 0° | 90° | 0° | 90° |
| (100) | ($\bar{1}$02) | 56±2° | 90° | 58° | 90° |
| (*hk*0) | (100) | 76(68–82)° | 90° | 75° | 90° |
| (001) | (011) | 141±5° | 33±2° | 139° | 31° |
| (*hkl*) | (111) | 118° | 54° | 119° | 53° |
| (*hk*0)* | (102) | 39° | 90° | 41° | 90° |
| (010)† | (001) | 0° | 90° | 0° | 90° |

For the interaxial angle $\beta$ in his orientation ($\gamma$ in the new anorthic orientation), Bøggild found 67–68°; we calculate 68·5°.

* Composition plane of twins about Bøggild's *c* [001] (new anorthic *b* [010]).
† Composition plane of twins across Bøggild's (010) (new anorthic (001)).

he anorthic cell and the *c*-face centred monoclinic pseudo-cell. The greement between the present results and Bøggild's provides further vidence for the correctness of the proposed cell. It also affords further vidence for the identity of the Bombay specimen with the type material.

### *Dehydration.*

Heller's X-ray studies showed that okenite changes to orientated vollastonite and unorientated cristobalite at 730° or above, the *b*-axis of he wollastonite coinciding in direction and approximately in length vith that of the okenite from which it was formed. They did not show vhether orientation was preserved in the sense of rotation around the -axis, and in an attempt to settle this point a portion of the present naterial was heated to 1000° and then examined in the electron micro- cope. The micrographs (pl. I, D) confirmed that the product consisted f pseudomorphs of the original material. The flakes had a slightly nottled appearance, and on close inspection some of them appeared to e broken into parallel fibres a few hundred Ångströms wide, lying along he fibre direction. The corresponding diffraction patterns (fig. 2*b*) howed distinct layer-lines perpendicular to the fibre direction, with a epeat distance of 7·26 Å. The even layer-lines consisted of relatively harp spots, but the odd ones consisted of streaks. There was always ome disorder in the direction of the fibre axis, which varied within each lake through a few degrees from the mean position. Flakes varied con- iderably in the degree of order as regards rotation around this axis. In ome cases, the distribution of spots along the even layer-lines was rregular, indicating that orientation around the fibre axis was probably andom, but others gave a pattern approaching that characteristic of a ingle crystal. That shown in fig. 2*b* is of the latter type. The even layers all on to a *c*-centred orthogonal net having $a = 15{\cdot}28$ Å., $b = 3{\cdot}63$ Å., vhich together with the presence of weak and streaky intermediate ayers agrees satisfactorily with wollastonite lying on (001). There was ome indication of the presence of Laue zones related to the *c*-spacing, ut these were too indefinite for measurement.

## Part II. Nekoite, a new mineral.

Eakle[1] described a mineral from Crestmore, California, which was haracterized by its chemical composition and optical properties as kenite. The specimen had been collected,[2] and some of the observations

[1] A. S. Eakle, Bull. Dept. Geol. Univ. California, 1917, vol. 10, no. 19, p. 327 M.A. 1–20].

[2] Private communication from W. F. Foshag, 20 July, 1952.

carried out by Dr. W. F. Foshag, who kindly made available a portion of the original material from the collection at the U.S. National Museum. It will be shown that the specimen was not okenite, but a new species, for which the name *nekoite* is suggested.

The specimen (U.S.N.M. 95637) consisted of a few fine, slender needles, up to 1 mm. long and 50 $\mu$ thick, and weighing in all about 0·1 mg. They were mixed with grains of calcite. This agrees with the original description.

Preliminary optical examination suggested that the needles showed parallel extinction, with very low birefringence, and mean refractive index 1·535. This agrees with the original description. On more detailed examination, however, it was seen that they showed repeated twinning, being composed of lamellae about 10 $\mu$ thick and lying parallel to the needle axis. A single lamella was detached and yielded the data given in table I. It will be seen that the apparent parallel extinction is a property of the twinned aggregates and not of the individual crystals.

### *X-ray examination.*

Oscillation and rotation photographs (fig. 1*b*) were taken about the needle or *b*-axis of a single lamella. Weissenberg photographs were also obtained for the (*h*0*l*), (*h*1*l*), (*h*2*l*), and (*h*3*l*) layers. The unit cell was thus found to be anorthic, with[1] $a$ 7·60, $b$ 7·32, $c$ 9·86 Å., $\alpha$ 111° 48′, $\beta$ 86° 12′, $\gamma$ 103° 54′; elongation *b*, cleavage (100). Pronounced pseudo-symmetry was observed. In oscillation photographs about *b*, the even layer-lines were relatively strong and showed an equatorial plane of symmetry, but the odd layer-lines were weak and showed no plane of symmetry. The pseudo-cell obtained by ignoring the odd layer-lines is thus monoclinic, and was found to be *c*-face centred with $a$ 14·78, $b$ 3·66, $c$ 9·15 Å., $\beta$ 91° 30′. The relation between the true cell and the pseudo-cell is shown in fig. 5. If all three axes of the pseudo-cell are doubled, all the reflections can be indexed on monoclinic axes.

Oscillation and Weissenberg photographs were also taken of the twinned aggregates about the needle axis. They showed that two orientations were present in approximately equal amounts. The even layer-lines in the oscillation photographs were identical with those given by single crystals, but additional reflections occurred in the odd layer-lines so that these also showed an equatorial plane of symmetry. In the

[1] This cell is not in the conventional orientation. Application of the transformation matrix $\|\bar{1}00/00\bar{1}/0\bar{1}0\|$ gives: $a$ 7·60, $b$ 9·86, $c$ 7·32 Å., $\alpha$ 111° 48′, $\beta$ 103° 54′, $\gamma$ 86° 12′; fibres parallel to *c*, cleavage (100).

Weissenberg photographs of the odd layers, the number of reflections along each line of constant $l$ was doubled, causing an apparent doubling of $a$. Together with the optical evidence, this indicates that twinning occurs either by rotation about $b$, or else by reflection across the plane perpendicular to it.

X-ray powder data, obtained using a 6-cm.-diameter camera, are given in table II. Resolution was not very high because of the small

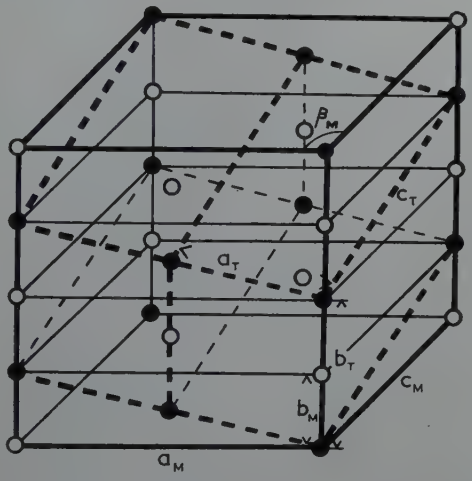


FIG. 5. Relation between the true unit cell of nekoite and the pseudo-cell. Full lines outline four $c$-face centred monoclinic pseudo-cells; broken lines complete the outlines of two anorthic unit cells. Full circles denote true lattice points; open circles denote additional lattice points pertaining to the pseudo-cell. Suffixes M and T denote parameters of the monoclinic and anorthic (triclinic) cells respectively.

amount of material available. The reflections were indexed by superposing single-crystal and powder photographs taken on the same camera; account was also taken of relative intensities observed on the Weissenberg photographs. Comparison of the observed and calculated spacings given in the table shows satisfactory agreement, thus affording confirmatory evidence for the correctness of the proposed unit cell.

*Goniometric data and unit-cell contents.*

Eakle stated that the crystals which he examined, although too slender for accurate measurement, appeared to be long prisms terminated by dull domes, and he considered them to be probably orthorhombic.

Approximate goniometric measurements by W. F. Foshag[1] gave the results quoted in table V, which shows also that each of the angles which he measured can be explained on the basis of the monoclinic, near orthorhombic, pseudo-cell of the present investigation. The number of different forms which must be assumed to occur would be reduced if,

TABLE V. Comparison of observed and calculated goniometric data for nekoite.

| | Observed (Foshag). | Calculated. |
|---|---|---|
| Prism axis: | Not stated; assumed to be $c$ | $b$ |
| Cleavage face: | Not stated; assumed to be (010) | (100) |
| Crystal system: | Probably orthorhombic | Monoclinic, $\beta$ 91° 30′ |
| | (110) $\wedge$ (1$\bar{1}$0) 33° 40′ | (102) $\wedge$ ($\bar{1}$02) 34° 24′ |
| | (010) $\wedge$ (011) 52° 0′ | (100) $\wedge$ (310) 53° 24′ |
| | (011) $\wedge$ (0$\bar{1}$1) 75° 0′ | (310) $\wedge$ ($\bar{3}$10) 73° 12′ |

as appears probable, the crystals examined by Foshag were twinned, but the data which he obtained are inadequate to settle this point. The matrix of the transformation from Foshag's axes to the monoclinic axes of the present investigation is $\|01\bar{2}/001/200\|$.

Calculation from the unit-cell dimensions found in the present investigation and Eakle's chemical analysis and specific gravity (2·206) yields the atomic cell-contents given in table III. They indicate that the ideal contents of the anorthic unit cell are $3[CaO.2SiO_2.2H_2O]$, or $Ca_3Si_6O_{21}H_{12}$.

Not enough material was available for a further analysis to be made in the present investigation, but as a qualitative and roughly quantitative check on the composition, a crystal of which the identity had been established by X-rays was heated to 900° C., and X-ray oscillation and rotation photographs then taken about the needle axis. These showed that the only crystalline dehydration product was a slightly disordered single crystal of wollastonite (or parawollastonite), with its $b$-axis parallel to the needle direction. This result indicates that the original crystal was a hydrated calcium silicate of fairly acid composition, in accordance with the analytical result.

## PART III. DISCUSSION.

The data presented in the first part of this paper show that okenite may be characterized by its chemical composition, optical properties, goniometric data and habit, X-ray powder data, and unit-cell dimen-

[1] In A. S. Eakle, loc. cit.

sions. There is adequate evidence that the data given for each of these relate to material substantially the same as that occurring at the type locality (Disko).

The results given in the second part show that the crystals from Crestmore that were examined were not okenite. The chemical compositions are the same, but significant differences exist in optical properties (table I), X-ray powder data (table II), X-ray rotation photographs about the fibre axis (fig. 1), and unit-cell dimensions (table I). Further evidence, independent of the present study, is provided by the fact that Foshag's goniometric data for the Crestmore material are quite unlike those obtained by Bøggild for okenite. In contrast, Foshag's data can be satisfactorily correlated with the present X-ray results for the Crestmore specimen. This provides additional evidence that the crystals from Crestmore that were examined in the present investigation were the same as those originally described, and makes it appear unlikely that any change had taken place in the material between the original examination and the present one.

The data obtained for the Crestmore specimen were compared with those of all the other known hydrated calcium silicates, both natural and artificial. They did not agree with any of them, except in the occurrence of a strongly fibrous habit with a repeat distance of about 7·3 Å. along the fibre axis. This is common to a number of anhydrous and hydrated calcium silicates, including the ones already mentioned.

Although the Crestmore material is not okenite, it shows certain similarities which are sufficiently close for the original characterization to be easily understood. Apart from the identical chemical compositions, the optical properties are relatively similar. The unit-cell dimensions, habits, and cell contents are also related; this is shown in table I. The cell of okenite is three times as large as that of the Crestmore mineral.

The crystal structures of the two minerals have yet to be determined. They are evidently fairly closely related to each other, and the behaviour on dehydration shows that they are also related to wollastonite. The electron-diffraction results on the dehydration of okenite show that there is a marked tendency towards an ordered transformation, in which the okenite *b*-direction becomes the wollastonite *b*-direction and the okenite (001) plane becomes, at least approximately, the wollastonite (001). The *b*-axis of okenite (7·20 Å.) is very near to that of wollastonite (7·27 Å.),[1] the okenite *c* (21·33 Å.) is almost exactly three times the wollastonite *c* (7·03 Å.), and the okenite *a* (9·84 Å.) somewhat greater

[1] B. E. Warren and J. Biscoe, Zeits. Krist., 1931, vol. 80 p. 391 [M.A. 5–186].

than the wollastonite $a$ (7·88 Å.). The unit cell of okenite contains the same number of silicon atoms (18) as three unit cells of wollastonite. These facts suggest that dehydration may occur by a process involving migration of calcium ions similar to that proposed in the case of afwillite,[1] each cell of wollastonite being formed in the present case from one-third of a cell of okenite.

The X-ray evidence on the dehydration of the Crestmore material showed that, as with okenite, the $b$-direction was unchanged on conversion into wollastonite. It also showed that the product was a single crystal and not an aggregate with random orientation around $b$, but did not allow the orientation to be determined relative to that of the initial material. It appears likely, by analogy with the case of okenite, that the (100) plane of the original material becomes the wollastonite (001), and that one unit cell of wollastonite, containing six silicon atoms, is formed from one of the initial material.

It follows from the foregoing that the Crestmore material must be regarded as a new species. Because of the likeness to okenite, the anagram *nekoite* is suggested.

*Acknowledgements.*—The early part of this work was carried out by one of us (H. F. W. T.) at Birkbeck College Research Laboratory, University of London. Thanks are due to Dr. L. J. Spencer for suggesting the name nekoite; to the Trustees of the British Museum and to Dr. W. F. Foshag and the U.S. National Museum for the specimens from Bombay and Crestmore respectively; and to Dr. H. G. Midgley for assistance with the optical determinations.

PLATE I. A. Electron micrograph of okenite. Positive print; specimen shadow-cast with Au–Pd alloy so that the length of the shadow is four times the thickness of the projecting material. B. Enlargement from A, showing several leaves each about 20 Å. thick. C. Enlargement from A, showing a sheet about 200 Å. thick with several flakes about 20 Å. thick lying on top of it. D. Electron micrograph of okenite after heating at 1000° C., showing the minutely fibrous character of the flakes.

[1] H. F. W. Taylor, Acta Cryst., 1955, vol. 8, p. 440.

J. A. GARD AND H. F. W. TAYLOR: OKENITE AND NEKOITE

# *The structures of the plagioclase felspars: VI. Natural intermediate plagioclases.*[1]

By P. Gay, M.A., Ph.D., A.Inst.P.

Department of Mineralogy and Petrology, Cambridge.

[Read 27 January, 1955.]

*Summary.*—Specimens from some forty different localities over the composition range from about 20 % An to about 70 % An have been examined by X-ray single-crystal methods. The majority of these specimens show the normal intermediate plagioclase pattern characterized by weak pairs of subsidiary layer-lines of variable separation. It has been found that the separation of these layer-lines is a linear function of composition over the whole composition range. Further, this range is found to extend to more soda-rich compositions than was formerly believed, whilst the limits of the range are approximately defined by the compositions at which the separations of the subsidiary layer-lines about either the *a*- or the *b*-axes become zero.

The anomalous patterns shown by some specimens are discussed, and it is shown that most of these may be interpreted in terms of the previous geological history of the specimens.

A comparison of the present results with those obtained by previous workers in this field is made, and it is shown how the principal points of difference may be resolved. An account of the phase relationships of the low-temperature plagioclase series is given, and the problems arising from the present work are discussed.

EARLY X-ray investigation of the plagioclases (Chao and Taylor, 1940) showed that there were three main structural divisions of the series: the albite structure, the anorthite structure, and the intermediate structure. The work described in this paper has been carried out as part of a programme of research to investigate the phase relationships of the plagioclase felspars, and is concerned with the intermediate structural region. Previous papers in this series have described in detail the results of an examination of lime-rich plagioclases. In one of these publications (Gay, 1953), a convenient grouping of all possible X-ray reflections into four classes was established: class (*a*) reflections are those with $(h+k)$ even, $l$ even; class (*b*) those with $(h+k)$ odd, $l$ odd; class (*c*) those with $(h+k)$ even, $l$ odd; class (*d*) those with $(h+k)$ odd, $l$ even; all indexing being carried out in terms of the unit cell of anorthite with a 14 Å. *c*-axis. Type (*a*) reflections, the principal reflections, are common

[1] Part V, Min. Mag., 1954, vol. 30, p. 428.

to all plagioclases; types (*b*), (*c*), and (*d*) are the subsidiary reflections, which distinguish the various structural arrangements. This classification will be adopted in the present publication.[1]

The most detailed examination of the intermediate structural region previously carried out has been described by Cole, Sörum, and Taylor (1951) and Sörum (1951). The diffraction pattern from an intermediate plagioclase is characterized by pairs of subsidiary reflections situated symmetrically about the layer-lines denoting the 14 Å. *c*-axis of anorthite; it appears that the type (*b*) reflections characteristic of body-centred anorthite have split into two. Doubled subsidiary reflections also appear symmetrically about the positions of the principal layer-lines in *a*- and *b*-axis photographs of these crystals. Cole *et al.* investigated the separation of these doubled subsidiary layer-lines as a function of the composition of the felspar. They expressed this separation in angular measure as a fraction of the spacing between the appropriate layers of the reciprocal lattice, successive layers being separated by 360°. $\delta_a$, $\delta_b$, and $\delta_c$, defined in this way, correspond to measurements made for a reciprocal lattice based on the albite-type structure—i.e. for the anorthite structures the values of $\delta_a$, $\delta_b$, and $\delta_c$ will be 0°, 0°, and 180° respectively. This terminology will be employed in this paper. Cole *et al.* showed that $\delta_a$, $\delta_b$, and $\delta_c$ were mutually dependent, and suggested a form of variation for each of these quantities with composition. They concluded that one boundary of the intermediate structure occurred near 72 % An and that the other was near 30 % An.

It was suggested by Chao and Taylor (1940) that the main features of these patterns can be explained in terms of a regular stacking of slabs of albite-like and anorthite-like material in the direction of the *c*-axis. More recently, Sörum (1951) has proposed a refined model of this type, in which the An-rich structure is identified with body-centred anorthite. A number of points are left unexplained by these treatments, and the present work suggests some simplifications of the structural problems. It is hoped to treat these in a later publication.

The work described by Cole *et al.* was in the nature of a review of the whole plagioclase series; the work to be described in this paper represents a detailed re-examination and amplification of their results for the intermediate structure. In particular the author has rechecked the data for specimens more basic than 50 % An, and examined a number of

[1] It should be noted that a similar classification has been used by Laves and Goldsmith (1951, 1954). In their nomenclature, the classes (*a*), (*b*), (*c*), and (*d*) become (*a*), (*b*), ($c_1$), and ($c_2$) respectively.

specimens less basic than 50 % An, a region for which the results of Cole *et al.* are extremely sparse; he has also tried to determine how the transition at the sodic end of the series to the albite structure occurs, and investigated whether the separation of the subsidiary reflections could be used as a determinative method for plagioclase composition. A systematic study of the effects of heat treatment on a number of natural plagioclases in this region will be described in another paper.

*Experimental methods.*

*Selection of material.*—Untwinned and unzoned single crystals were used as far as possible. Many of the materials from which the specimens were selected had been chemically analysed; for such specimens, the grains selected were known from their optical properties to be typical of the bulk material, and it has been assumed that their composition corresponds to that of the bulk material. For specimens for which no analysis was available, optical determinations were made either from refractive indices (using the curves of Chayes, 1952) or from universal-stage measurements, usually on the fragment used for the X-ray work. Optical determinations of this kind were also made as a check on critical specimens even when their bulk composition was known from analysis. These methods were preferred to melting the crystal and determining the refractive index of the glass, principally because the crystal remains intact. The accuracy of determination is probably $\pm 2$ % An at the worst, which is adequate for the present work, and is probably as good as can be obtained without resort to complicated experimental techniques.

In their previous work Cole *et al.* used a number of specimens selected apparently at random from a particular source material. The composition of each of these fragments was then determined by measurement of the extinction angles on the cleavage faces. These extinction angles are quoted to 0·1°, which seems to be an overestimate of the accuracy with which such angles can be determined. Further, the compositions were then derived using the curves of Rogers and Kerr (1942). Comparison of similar curves published by other authors shows that there are appreciable discrepancies among them, and it is difficult to assess the reliability of any one set of curves. Hence it seems that the accuracy of determination of $\pm\frac{1}{2}$ % An quoted by Cole *et al.* is again an overestimate.

It is probable that the methods adopted in the present work are more satisfactory. The optical curves used appear to have a sounder basis

than those of extinction angles. Further, it is thought that the refractive indices, in particular, change very little with heat treatment. This would minimize any error due to the use of inverted and partially inverted specimens, a point mentioned by Cole *et al.*

*X-ray methods.*—Single-crystal oscillation and Weissenberg methods have been exclusively used. The axis of oscillation has usually been one of the principal axes, although other axes have sometimes been used for confirmatory purposes. The oscillation photographs were used for the detection and the determination of the separation of the subsidiary layer-lines, and the Weissenberg photographs for the determination of the positions of the subsidiary reflections in reciprocal space.

*Measurement of the separation of the subsidiary layer-lines.*—Linear measurements of the separation between subsidiary reflections were made, using either a travelling microscope or a device employing two sliding, mutually perpendicular scales (similar to that shown on p. 226, Buerger, 1942). It was found that the former was satisfactory for sharp, relatively strong spots, whilst the latter was most usefully employed on the diffuse or weak reflections. The separations in reciprocal space were then calculated from the linear measurements.

The accuracy of measurement necessarily depends on the quality of the spots, which depends in part on the composition of the specimen. Cole *et al.* claim that an accuracy of $\pm 1°$ in $\delta_a$, $\delta_b$, $\delta_c$ (or $\frac{1}{360}$ of the separation of the principal layer-lines) is achieved *at the worst*; the agreement between the calculated and experimental measurements of separations for axes other than the principal axes which they quote is extremely good. The present author has not been able to reproduce this accuracy; the standard deviation calculated from a number of measurements on each specimen is usually *at the best* $\pm 1°$, and often very much worse. The measurements of $\delta_a$, $\delta_b$, and $\delta_c$ which have been made are quoted with the appropriate standard deviation. In considering the probable accuracy of measurement it should be noted that the majority of the specimens used by Cole *et al.* were in the composition range where the subsidiary diffraction spots are strong and sharp.

## *Specimens.*

A list of the materials used together with the bulk chemical composition and occurrence is given in table I; wherever possible, references to previous descriptions and work on the material used have been included. The specimens included in this table all fall roughly within the composition range over which the characteristic intermediate pattern is found.

TABLE I. List of specimens.

| No. | Locality. | Occurrence. | An/An+Ab (Mol. %). | References. |
|---|---|---|---|---|
| 1 | Lincoln Co., Wisconsin. | Anorthosite | 73 | 5(24); 6(23). |
| 2 | Duluth, Minnesota. | Gabbro | 71 | 5(8); 6(22). |
| 3 | Wichita Mts., Oklahoma. | Orthoclase-quartz-gabbro | 70 | 5(5); 6(20). |
| 4 | Chester Co., Pennsylvania. | Diabase | 67 | 5(18); 6(18). |
| 5 | Clear Lake, Utah. | Phenocrysts | 65 | 15(7). |
| 6 | Stillwater, Montana (EB 40). | Gabbro | 64 | — |
| 7 | St. John's Pt., Co. Down, Ireland. | Phenocrysts in basalt | 63 | 12; 1; 19. |
| 8 | Shelby, N. Carolina. | Hornblende-gabbro | 60 | 5(17); 6(16). |
| 9 | Naine, Labrador. | ? | 58 | 3(E). |
| 10 | Naine, Labrador. | ? | 56 | — |
| 11 | New Amalfi, South Africa. | Dolerite | 55 | 19. |
| 12 | Skaergaard, E. Greenland. | Hypersthene-olivine-gabbro | 53* | 25(2307). |
| 13 | Isle of St. Paul, Labrador. | ? | 53 | 15(6). |
| 14 | New Amalfi, South Africa. | Dolerite | 51 | 20(EH20); 19. |
| 15 | Skaergaard, E. Greenland. | Middle gabbro | 50* | 25(1691). |
| 16 | Essex Co., New York. | Anorthosite | 50 | 5(4); 6(9). |
| 17 | Sipoo, Uudenmaan, Finland. | ? | 47* | — |
| 18 | New Amalfi, South Africa. | Dolerite | 46 | 20(EH52); 19. |
| 19 | Monte Rosso, Linosa (B.M. 1924, 914). | Crystal lapilli | 46* | 7; 19. |
| 20 | Skaergaard, E. Greenland. | Middle gabbro | 45* | 25(3661). |
| 21 | Skaergaard, E. Greenland. | Ferrogabbro | 45* | 25(3655). |
| 22 | Beaver Bay, Minnesota. | Diabase | 44 | 11; 19. |
| 23 | Skaergaard, E. Greenland. | Ferrogabbro | 41 | 25(2580); 26. |
| 24 | NW. of Agay, Esterel, France. | Andesite | 40* | 14; 19. |
| 25 | Skaergaard, E. Greenland. | Ferrogabbro | 40* | 25(1907). |
| 26 | Crestmore, California. | Granodiorite | 38 | 5(19); 6(8); 16(16). |
| 27 | Sierra Nevada, California. | Granodiorite | 38* | — |

TABLE I (*cont.*)

| No. | Locality. | Occurrence. | An/An+Ab (Mol. %). | References. |
|---|---|---|---|---|
| 28 | Skaergaard, E. Greenland. | Ferrogabbro | 37 | 25(4145); 26. |
| 29 | Yosemite Valley, California. | Hornblende-bastite-quartz-monzonite | 37* | — |
| 30 | Skaergaard, E. Greenland. | Ferrogabbro | 37* | 25(4146). |
| 31 | San Luis Obispo Co., California. | Dacite | 36 | 5(11); 6(7). |
| 32 | Spanish Peak, California. | Gneissoid granodiorite | 35 | 5(21); 6(6); 16(14). |
| 33 | Knoydart, Scotland. | Garnet-mica-schist | 35* | — |
| 34 | Santa Maria, Guatemala (Oct. 1902 eruption). | Pumice | 33* | — |
| 35 | N. Morar, Inverness-shire, Scotland. | Garnet(?)-mica-schist | 32* | — |
| 36 | Macon Co., N. Carolina. | From a vein of talc-antho-phyllite-vermiculite-plagioclase cutting dunite. | 30 | 6(28). |
| 37 | Head of Little Rock Creek, Mitchel Co., N. Carolina (97490). | Coarse crystals from pegmatite | 30 | 15(11). |
| 38 | Hawk Mica Mine, Bakersville, N. Carolina (81065). | Crystals from pegmatite | 23 | 15(10). |
| 39 | Hawk Mica Mine, N. Carolina (103086). | Crystals from pegmatite | 22 | 15(9). |
| 40 | South Carolina (81822). | Greenish clear crystals from pegmatite | 17 | 15(8). |

*Notes.*—All compositions in this table were calculated from analyses, except those marked *, which were determined optically. The bulk compositions of specimens 27, 29, 33, and 35, and the composition of the single fragment of specimen 34 used in the X-ray work were determined by Dr. I. D. Muir.

In the reference column the unbracketed numbers refer to the list of references at the end of this paper; the numbers or letters within an associated bracket are those given to the particular specimen by the quoted author. Of the specimens for which no reference is quoted, no. 6 was received from Professor H. H. Hess, 10 from Professor C. D. Jeffries, 33 and 35 from Mr. R. St. J. Lambert; specimen 34 is to be described in a forthcoming paper by Drs. Merwin and Zies.

A number of other specimens beyond the limits of this composition range have been examined; these are not listed in the table, but relevant

aspects of the results on these specimens will be quoted in the later discussion. A full description of these results will be given in another publication.

*Experimental results and discussion.*

In this section it is convenient to discuss first the diffraction patterns from low-temperature intermediate plagioclases that show similar characteristic features; these will be called 'normal' patterns. The 'anomalous' patterns that do not conform to the scheme for the normal specimens are discussed afterwards.

Felspars with the normal intermediate structure give diffraction patterns showing the characteristic doubling of the type (*b*) reflections. As noted by Cole *et al.* these reflections usually occur in pairs, although sometimes one member of a pair may be absent or undetected.

It was suggested in the earlier work that the separation of the subsidiary reflections was simply related to the composition of the fragment, and that the separations about the three principal axes were not independent. In table II are listed the measured values of the angular separations $\delta_a$, $\delta_b$, and $\delta_c$ for as many specimens as possible. It will be noted that for a number of specimens no values have been recorded; for these no subsidiary reflections were observed. For other photographs, although the subsidiary reflections may be present, they are of such poor quality that no reliable measurement could be made. In fig. 1, $\delta_a$ and $\delta_b$ are plotted against $\delta_c$, and in fig. 2, $\delta_a$, $\delta_b$, and $\delta_c$ are plotted independently against the anorthite content of the specimen. In fig. 1, it is seen that $\delta_a$ and $\delta_b$ are linearly dependent on $\delta_c$, whilst from fig. 2 it is seen that all three quantities vary linearly with composition to within the accuracy of the experimental measurements.

TABLE II. Measurements of separations of subsidiary reflections.

| No. | % An. | $\delta_a$. | $\delta_b$. | $\delta_c$. | Remarks. |
|---|---|---|---|---|---|
| 1 | 73 | — | $37\pm2°$ | $165\pm1°$ | Diffuse (*c*) spots with intermediate pattern. |
| 2 | 71 | — | — | — | Diffuse (*c*) spots with body-centred anorthite pattern, i.e. anorthite D pattern (Gay, 1953). |
| *3 | 70 | — | $43\pm2°$ | $163\pm1°$ | — |
| 4 | 67 | $9\pm3°$ | $35\pm2°$ | $157\pm1°$ | — |
| *5 | 65 | — | — | — | †Very diffuse single (*b*) spots of body-centred anorthite present. |
| *6 | 64 | $8\pm2°$ | $33\pm1°$ | $159\pm\frac{1}{2}°$ | † — |
| 7 | 63 | — | — | — | Very diffuse single (*b*) spots of body-centred anorthite present. |

TABLE II (*cont.*)

| No. | % An. | $\delta_a$. | $\delta_b$. | $\delta_c$. | Remarks. |
|---|---|---|---|---|---|
| 8 | 60 | $14\pm2°$ | $28\pm1°$ | $146\pm1°$ | — |
| 9 | 58 | $12\pm2°$ | — | $151\pm1°$ | *b*-axis not observed. |
| *10 | 56 | $23\pm1°$ | $17\pm2°$ | $141\pm1°$ | Very diffuse weak reflections in addition to normal pattern. |
| *11 | 55 | $16\pm2°$ | $18\pm2°$ | $148\pm1°$ | — |
| *12 | 53 | $18\pm2°$ | $21\pm2°$ | $145\pm1°$ | — |
| *13 | 53 | $25\pm1°$ | $20\pm2°$ | $145\pm1°$ | ‡ — |
| 14 | 51 | $20\pm1°$ | $17\pm2°$ | $138\pm2°$ | Split (*b*) spots rather weaker than expected. |
| *15 | 50 | $25\pm2°$ | $21\pm2°$ | $141\pm1°$ | ‡ — |
| *16 | 50 | $24\pm2°$ | $19\pm2°$ | $139\pm1°$ | — |
| 17 | 47 | $28\pm1°$ | $13\pm1°$ | $132\pm2°$ | — |
| *18 | 46 | — | — | $\sim 132°$ | Split (*b*) spots barely visible. |
| *19 | 46 | — | — | — | No (*b*) spots. |
| *20 | 45 | $23\pm2°$ | $19\pm2°$ | $136\pm1°$ | — |
| 21 | 45 | $23\pm3°$ | $15\pm2°$ | $136\pm1°$ | — |
| *22 | 44 | — | — | — | No (*b*) spots. |
| 23 | 41 | $27\pm4°$ | $14\pm2°$ | $132\pm2°$ | Split (*b*) spots slightly weaker than expected. |
| 24 | 40 | — | — | — | No (*b*) spots. |
| 25 | 40 | $31\pm3°$ | $9\pm2°$ | $125\pm2°$ | Split (*b*) spots definitely weakened, slightly diffuse. |
| 26 | 38 | $31\pm3°$ | — | $128\pm3°$ | Split (*b*) spots slightly diffuse. *b*-axis not observed. |
| 27 | 38 | $33\pm4°$ | 8° | $125\pm4°$ | Split (*b*) spots diffuse. |
| *28 | 37 | — | — | — | No (*b*) spots. |
| 29 | 37 | $32\pm3°$ | $9\pm3°$ | $121\pm4°$ | Split (*b*) spots slightly diffuse. |
| *30 | 37 | — | — | — | No (*b*) spots. |
| *31 | 36 | — | — | — | No (*b*) spots. |
| *32 | 35 | $30\pm5°$ | $7\pm3°$ | $128\pm4°$ | Split (*b*) spots quite diffuse. |
| 33 | 35 | — | — | — | Split (*b*) spots too diffuse to be measured. |
| 34 | 33 | — | — | — | No (*b*) spots. |
| 35 | 32§ | $43\pm7°$ | — | $113\pm5°$ | Split (*b*) spots very diffuse. |
| 36 | 30 | $\sim 38°$ | — | $118\pm7°$ | Split (*b*) spots very diffuse. |
| 37 | 30 | $42\pm5°$ | $\sim 4°$ | $120\pm6°$ | Split (*b*) spots very diffuse. |
| 38 | 23 | — | — | $\sim 121°$ | Split (*b*) spots very diffuse. |
| 39 | 22§ | $\sim 43°$ | — | $\sim 120°$ | Split (*b*) spots extremely diffuse. |
| *40 | 17§ | — | — | $\sim 100°$ | Split (*b*) spots extremely diffuse. |

* Indicates that more than one crystal has been examined. The values quoted for $\delta_a$, $\delta_b$, and $\delta_c$ are average values for all observations.

† Photographs of some specimens of these materials were taken by Dr. S. W. Bailey, University of Wisconsin.

‡ Some specimens of these materials were examined and the measurements of separations made by Mr. C. J. E. Kempster, Cavendish Laboratory, Cambridge.

§ The anorthite contents of the fragments used of these three specimens were determined from their refractive indices by Mr. J. D. C. McConnell; anorthite contents of $28\pm3$ %, $21\pm3$ %, and $23\pm2$ % were obtained for specimens 35, 39, and 40 respectively.

The quality of the type (*b*) spots is very variable. The doubled spots can be almost as sharp as the principal reflections, or extremely diffuse so that they can only be seen on very heavily exposed photographs; they can also show diffuse 'tails'. In the main, normal specimens in the composition range from about 70 % An to 40 % An show the sharp, relatively strong doubled reflections; more sodic specimens show these reflections becoming increasingly diffuse with soda content until at around 20 % An the original reciprocal points occupy very large volumes of reciprocal space. In this latter region measurements of the relative separations become increasingly more inaccurate. The doubled type (*b*) reflections which are present are derived by a systematic splitting of the type (*b*) reflections observed for body-centred anorthite. It also appears to be generally true that the intensities of the split reflections are comparable with those of the corresponding reflections in the body-centred anorthite pattern, i.e. a strong (*b*) reflection in body-centred anorthite is usually replaced by a relatively strong pair of split reflections in the intermediate pattern. It appears, however, that the intensities of the two components of any one pair are different (in agreement with Sörum, 1951, and Cole *et al.*, 1951). The intensities of corresponding (*b*) reflections measured relatively to the intensities of nearby principal reflections appear to change very little over the range 70 % An to 40 % An; it is difficult to be certain whether this remains true for the more sodic specimens owing to the rapidly changing diffuse character of the reflections. No systematic measurements of the changes in intensity of the principal reflections over the composition range have been made; it seems certain that some changes do occur that would be revealed by a detailed study, but they are small and are not immediately obvious on the photographs.

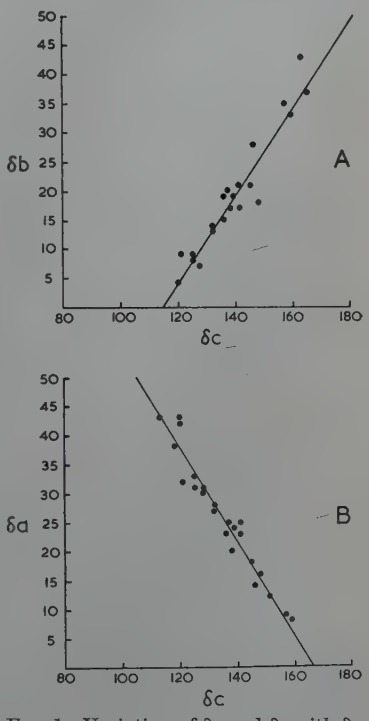


Fig. 1. Variation of $\delta_a$ and $\delta_b$ with $\delta_c$.

The preceding paragraphs establish the changes that occur in the diffraction patterns of low-temperature series of plagioclases between about 20–25 % An and 70–75 % An. At the more basic limit there

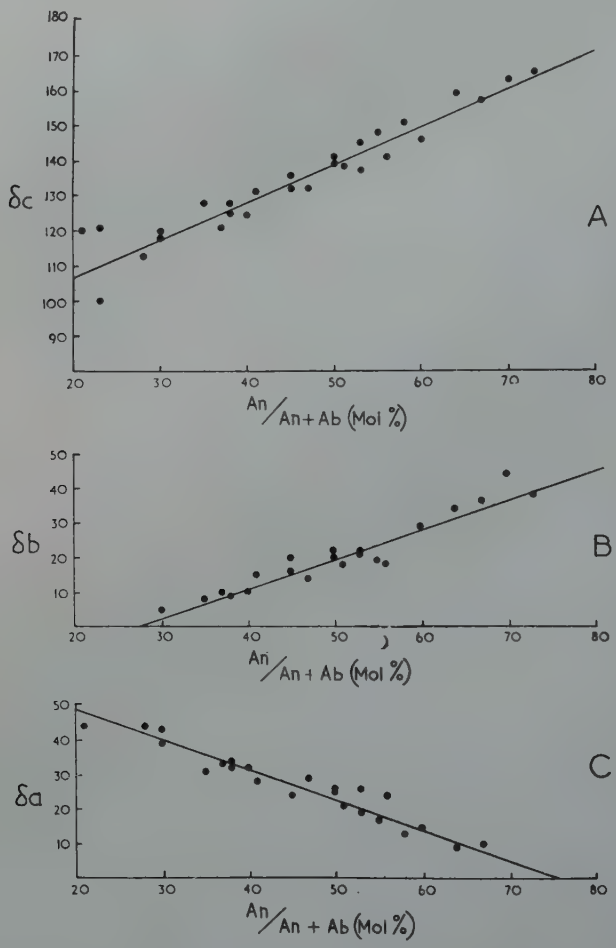


FIG. 2. Variation of $\delta_a$, $\delta_b$, and $\delta_c$ with chemical composition.

appears to be a sharp termination to the normal intermediate pattern somewhere in the region between 70–75 % An, after which it is apparently replaced by a body-centred anorthite pattern with single type (*b*) reflections. As the albite content increases from this limit the mutually dependent separations of the subsidiary layer-lines vary linearly with

composition over the whole range without much change in the intensities of corresponding reflections. At about 40 % An the subsidiary reflections become diffuse, the degree of diffuseness increasing with albite content. At this end of the composition range there is no sharp limit except that provided around 20 % An by the occurrence of the unmixed structure of the peristerite type (Laves, 1954). For all specimens in this composition region not peristeritically unmixed which have been examined so far the diffuse intermediate reflections have been found.

An interesting feature of the curves shown in fig. 1 is that when $\delta_a = 0$, $\delta_c \sim 167°$, and when $\delta_b = 0$, $\delta_c \sim 115°$. If these two values of $\delta_c$ are interpolated on the appropriate curve in fig. 2, they correspond to An contents of approximately 28 % An and 75 % An, i.e. roughly the limits of the region over which the intermediate structure is found. It appears that for a stable intermediate structure the separations of the reciprocal points corresponding to the doubled subsidiary type (*b*) reflections parallel to the crystallographic axes must all be finite. Further discussion of the reciprocal lattice geometry of the intermediate patterns will be given in a later paper.

Specimens 3, 4, 6, 8, 9, 11, 12, 13, 15, 16, 17, 20, 21, 26, 27, 29, 32, 33, 35, 36, 37, 38, 39, and 40 show patterns which are consistent with the normal behaviour outlined above. The diffraction patterns of specimens that do not conform to the scheme described above are dealt with next.

One group of specimens (nos. 19, 22, 24, 28, 30, 31, and 34) shows no subsidiary type (*b*) reflections; only the principal reflections are present and the pattern corresponds to that from an albite-type structure. From the results of the heat-treatment experiments to be described in another paper, such patterns are known to be indicative of a high-temperature structural state. The optical properties of some of the specimens mentioned above (those from Beaver Bay, Linosa, and Esterel) have been determined by universal-stage methods by Muir (1955). He considers that the felspars from Beaver Bay and Esterel show transitional optics lying between the low- and high-temperature values; the optical properties may be changed by heating until they are nearly the same as those of the ultimate high-temperature state. This is quite consistent with the present interpretation since it is to be expected that the high-temperature structural state (with the albite pattern), as distinct from the low-temperature state (with the normal intermediate pattern), can exist over a wide temperature range. The felspar from Linosa was selected by Köhler (1941) as one of his standard high-temperature specimens.

The patterns from specimens 5 and 7 are rather similar; the split type (*b*) reflections are not present. On heavily exposed photographs there is a weak diffuse region of blackening midway between the principal *c*-axis layer-lines; there is no apparent tendency for a separation into two discrete reflections, and the spots are like very diffuse odd layer-line reflections from body-centred anorthite. These patterns have been commented on before (Cole *et al.*, 1951; Gay and Taylor, 1953). Formerly it was thought that the material from which specimen 5 was taken showed no subsidiary reflections, but a very careful examination has shown that its pattern is similar to that of 7 in showing the single diffuse subsidiary reflections. Undoubtedly these anomalous patterns are due to some special feature of the environment of these specimens, and the patterns are similar to those found for a nearly high-temperature specimen obtained by heating a low-temperature material. The optical properties of the St. John's Point material have been commented on by Muir (1955), who described it as having transitional optics.

Another type of anomalous pattern is that which is given by some of the more basic specimens, in which the diffuse type (*c*) reflections occur. Specimen 2 shows a body-centred anorthite pattern (which is not surprising since the bulk composition is in the border region) plus diffuse type (*c*) reflections and is thus the D pattern of anorthite (Gay, 1953). Specimen 1 shows the type (*c*) reflections occurring together with the split type (*b*) reflections. In a previous publication (Gay, 1953) bytownites containing approximately 70 % An and 80 % An were examined and it was found that type (*c*) reflections were absent; it was thought that specimens containing more than about 15–20 % Ab did not show these reflections. More recently Laves and Goldsmith (1954) have described specimens containing up to as much as 27 % Ab in which these reflections are still present. In two of their specimens the type (*b*) reflections were present and single, whilst in a third these reflections were split with a separation of $\delta_c \sim 167°$. This latter pattern is similar to that which is found for specimen 1. It is possible that specimen 10 shows a similar pattern, though for this specimen the diffuse reflections are so weak that it is impossible to decide with certainty the class to which they should be allocated. It seems probable that the diffuse regions on these photographs must be due to some other cause, since, as stated by Laves and Goldsmith, the (*c*) reflections for specimens between 70–75 % An are on the limit of observation.

The specimens from the layered series of New Amalfi and Skaergaard

are particularly interesting. For the New Amalfi sheet, the pattern from the most basic specimen is quite normal. The next specimen (no. 14) shows an almost normal intermediate pattern appropriate to its composition; however, if a careful examination is made it is found that when the subsidiary reflections are compared with those given by specimens from different localities but with similar compositions, they seem to be rather weaker than expected. The third New Amalfi plagioclase (no. 18) shows only a few very feeble subsidiary reflections, which, however, are present in the normal positions on the *c*-axis photographs. This suggests that the three specimens show evidence for a change of structural condition in the series, changing from a normal low-temperature material (no. 11) to a partially inverted state, which is almost that of the high-temperature structural form, for the most sodic specimen examined (no. 18). Muir (1955) has examined the optical properties of these three specimens and has reached similar conclusions; he has also been able to relate satisfactorily the state of the plagioclase to the exsolution and inversion of the associated pyroxenes. Specimens from the layered series of the Skaergaard intrusion show a similar trend. Specimens 12, 15, 20, and 21 show quite normal low-temperature patterns, but in those from specimens 23 and 25 there is a weakening of the intensities of the subsidiary reflections; the still more sodic specimens (nos. 28, 30) appear to have gone over completely into the high-temperature structural state. A complete account of X-ray and optical studies of these and other plagioclases from the Skaergaard intrusion and their relationships to the associated pyroxenes is in preparation by Muir and the present author. One immediate comment that can be made is that, although these layered series provide an extremely fine variation of felspar composition over a particular range, caution must be exercised if specimens from these (and possibly other) intrusions are to be used as samples for the determination of standard plagioclase properties.

One small anomaly which can occur in the diffraction patterns is worthy of note although it is not of fundamental importance. If the fragment used is strongly zoned, the subsidiary reflections are found to have 'tails'. The spots are present in positions corresponding to the composition of the main body of the crystal, but the tails associated with these spots show the zoning.

On some photographs, reflections not coming within the description above are seen; these will be discussed at the appropriate point in the next section, where a comparison with previous work will be made.

*Comparison with previous work.*

The earliest X-ray work on the intermediate plagioclases (Taylor, Darbyshire, and Strunz, 1934; Chao and Taylor, 1940) described the diffraction pattern; Chao and Taylor suggested a model by which the main characteristics of the diffraction effects could be explained. In both cases, however, only a small number of specimens was examined. A full account of the intermediate pattern was given by Cole *et al.* (1951) and Sörum (1951), using a suite of felspars provided by Professor R. C. Emmons. It is interesting to compare this later work with that described here, particularly since there are several points of difference, which will be discussed here. I am indebted to Dr. W. H. Taylor and H. Sörum for making available to me photographs taken during this previous investigation for re-examination in the light of the present work.

One of the principal points at issue concerns the variations of the separations $\delta_a$, $\delta_b$, and $\delta_c$ with chemical composition. It should be stressed that the magnitudes of $\delta_a$, $\delta_b$, and $\delta_c$ were not all recorded for all specimens by Cole *et al.*, and hence their data were less complete than those recorded here. For plagioclases containing more than 50 % An there is good agreement. For specimens with less than 50 % An Cole *et al.* tentatively suggested that the variations take the form of straight lines symmetrically about 50 % An with respect to the linear variations for the more basic specimens. Some evidence for this suggestion was provided by data from the three specimens they examined in this region. The present investigations show that this suggestion is incorrect and that the variations are linear (as far as it is possible to determine) over the whole range. It remains to explain the occurrence of the three points below 50 % An plotted by Cole *et al.* For two of these, both from the same material from Emmons's suite (no. 16 in the present work), there is no difficulty. The values recorded for one of these two (sample 4, specimen 1, Cole *et al.* numbering) are substantially in agreement with those found for a representative specimen from the same sample by the author. For the second specimen from the same sample, the author has remeasured the original photographs with the result that the previously recorded values of $\delta_c$ and $\delta_a$ lie within the standard deviation of the new measurements; they are very little different from those of the typical specimen. However, the composition recorded by Cole *et al.* for this specimen was derived from measurements of extinction angles on the cleavage faces, which are quoted as $\sim 10°$

on (010) and 2·9° on (001). Apart from any question of the accuracy of these measurements, these angles lead to compositions $\sim 43$ % An and $\sim 35$ % An, using the extinction-angle curves of Rogers and Kerr (1942) (which were used by Cole *et al.*). There is clearly some confusion or inaccuracy in the optical measurements of Cole *et al.*, and their observations on this material should be discarded.

Such considerations cannot be applied to the third specimen (sample no. 11, specimen no. 1, Cole *et al.* numbering). Several specimens of material from the same source (no. 31) have been examined and no trace of the normal intermediate reflections, which would have become a little diffuse in this composition range, has been found. This suggests that the felspar is in the high-temperature structural state. Some confirmation of this is given: by its occurrence in a dacite (a rock type in which high-temperature optics have been found (van der Kaaden, 1951); and by the work of Smith (1956) who has found that the reciprocal lattice parameters for material from the same source are intermediate between the curves of reciprocal lattice parameters for felspars from low-temperature sources (pegmatites) and synthetic felspars. It seems likely, therefore, that the few exceedingly weak reflections with $\delta_c \sim 160°$ reported for this specimen by Cole *et al.* cannot be the normal intermediate subsidiary reflections but must arise from some secondary cause; hence this point also must be disregarded.

Other specimens in this sodic region used in the present work which have been mentioned in other X-ray investigations are nos. 26 and 32. These have been examined by Cole *et al.* (numbered sample 19, specimen no. 2, and sample 21, specimen no. 1) and by Laves (1954) (nos. 16 and 14); both these investigations recorded that the patterns showed a homogeneous felspar. Both the specimens examined by the author showed the normal intermediate pattern for this composition range, i.e. one in which the type (*b*) reflections are beginning to become diffuse. It seems probable that these reflections were not observed either by Laves or by Cole *et al.* owing to insufficient exposure times. Cole *et al.* noted that *c*-axis photographs of their specimen numbered 19 showed reflections 'off the principal layer-lines, but not in positions corresponding to pairs of subsidiary layer-lines as in other intermediate plagioclases'. On re-examination, one of these original photographs shows very faintly the normal intermediate reflections; it is not clear if these were the reflections referred to by Cole *et al.*

Some specimens in the albite-oligoclase region (including some of the Emmons specimens common to both Laves and Cole *et al.*) have been

examined. In agreement with Laves, it is found that these specimens are unmixed into two phases; often, however, the detection of the unmixing is very difficult when using only oscillation methods. Re-examination of the photographs taken by Cole *et al.* of their specimens numbered 3, 9, and 22 shows that the unmixing is detectable in nos. 3 and 22. Laves notes that specimen no. 9 has 'frozen' in the process of unmixing, which probably accounts for the apparent homogeneity of the oscillation photographs.

Turning to the more basic specimens, in which diffuse type (*c*) reflections occur, re-examination of the Cole *et al.* photographs shows that they can be observed on those from specimens nos. 23 and 25 (Cole *et al.* numbering). On the pattern from no. 23 they are present but very weak, with sharp single type (*b*) subsidiary reflections; on the pattern from no. 25 they are present with doubled type (*b*) subsidiary reflections (cf. description of pattern from specimen no. 1, present investigation; this material is listed by Cole *et al.* (no. 24), but no description of the pattern is given). Material from specimen no. 25 was also used by Laves and Goldsmith (1954), who describe the occurrence of type (*c*) reflections with single type (*b*) reflections. These authors also examined materials from samples nos. 1 and 2 (Cole *et al.* numbering) and report that for specimen no. 1 they could observe type (*c*) reflections after extremely heavy exposures, whilst under similar conditions these were not shown by no. 2. These reflections are not visible on any of the photographs taken by Cole *et al.* of specimens from these materials, but this is probably due to lack of exposure.

In the course of the present work it has been necessary to take many very heavily exposed photographs. On some of these photographs extremely weak reflections not of the normal subsidiary type have been observed. It appears likely that these reflections are associated with some secondary cause due to the plagioclase structure itself, and cannot be ascribed to some external factor such as twinning, imperfect single crystal, &c. On some photographs the additional subsidiary reflections, in pairs close to and symmetrical about the principal reflections, that were mentioned by Cole *et al.* have been observed. Further, quite often associated with the strongest of the principal reflections are found diffuse 'tails' along lines of constant $\theta$. These secondary effects have been ignored in the present study, which sought to deal with the main subsidiary reflections; some light may be thrown upon their occurrence when a satisfactory explanation of the main subsidiary reflections has been devised.

*Summary and conclusions.*

Over a large composition range the low-temperature plagioclases are characterized by the normal intermediate pattern. In such patterns, in addition to the main type (*a*) reflections, subsidiary reflections, often occurring in pairs, replace the single subsidiary type (*b*) reflections found in basic plagioclases. The angular separations of these subsidiary reflections vary linearly with composition over the whole composition range. At the basic limit ($\sim$ 70–75 % An) $\delta_a$ is approximately zero, whilst the sodic limit ($\sim$ 20–25 % An) appears to occur at the composition for which $\delta_b$ becomes zero; more sodic specimens show peristeritic unmixing. The subsidiary reflections are relatively sharp over the region from 70 % An to 40 % An; rough estimates of the intensities of corresponding reflections show that they change very little (if at all) over this range. Within the range from about 40 % An to 20–25 % An the subsidiary reflections become more diffuse the more sodic the felspar.

It is possible to use the separation of the subsidiary reflections to determine the plagioclase composition. Probably the $\delta_c$ variation would be the most suitable to use, although the *c*-axis is usually the most difficult to locate. On specimens between 70 % An and 40 % An it is probable that with careful work $\delta_c$ could be determined to $\pm 1°$; using the present curve this would lead to an accuracy of about $\pm 1$ %. This is probably better than all but the most careful optical work. It should be realized, however, that in such determinations any other factors (e.g. the orthoclase content of the plagioclase) which may affect the positions of the subsidiary reflections are not taken into account. Below 40 % An, where the reflections become diffuse, it would be considerably less accurate than this. It seems hardly likely that this method would be of much petrological use, since although it offers greater accuracy than routine optical measurements it is rather more difficult to carry out and of necessity is performed on only one crystal. It should be noted, however, that the method is independent of the state of inversion of the felspar provided, of course, that the subsidiary reflections can still be observed; this will be fully dealt with in a later publication.

Whilst the majority of the specimens examined showed the normal intermediate pattern, other specimens give anomalous patterns, which may be ascribed to the different structural conditions of the felspars, arising probably from their particular geological environments; some supporting optical data have been quoted and further evidence will be given in a later paper on the heat treatment of these felspars.

Low-temperature plagioclase felspars appear to show a very limited region of existence for the homogeneous low-albite structure, probably over a composition range from $An_0$ to $An_{1-5}$. All low-temperature specimens (i.e. the completely stable structural forms) lying in composition between $An_{1-5}$ and $An_{70-75}$ are unmixed. Those between $An_{1-5}$ and $An_{20-25}$ are unmixed into soda-rich and calcium-rich components,

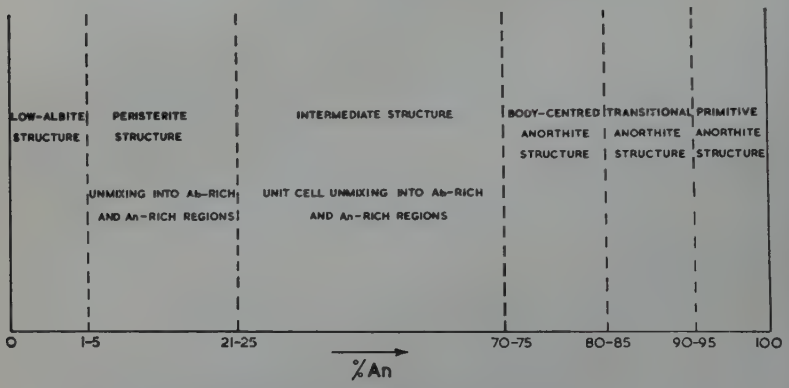


FIG. 3. Schematic representation of the structural types distinguished in low-temperature plagioclase felspars.

usually on a sub-microscopic scale. Nevertheless, the X-ray patterns from the two phases can be detected (Laves, 1954; Gay and Smith, 1955). If the explanation of the intermediate diffraction patterns in terms of an ordered superlattice of soda-rich and calcium-rich regions is accepted, it may be said that the intermediate structures between $An_{20-25}$ and $An_{70-75}$ are unmixed; for these, however, the unmixing is on a unit-cell scale, and is of a different character from that in the albite-oligoclase region. Bytownites and anorthites in the low-temperature state can show the body-centred, transitional, and primitive anorthite arrangements depending apparently on their composition. A schematic representation of the probable composition ranges of the different structural modifications distinguished in low-temperature plagioclases is shown in fig. 3.

The calcium-rich phase of unmixed albite-oligoclase is of interest, for so far it has only been detected as a component phase in two-phase specimens. All specimens which have been examined in the 15–30 % An region have shown either the normal intermediate pattern or the dual pattern of a two-phase specimen. This suggests that the peristerite and

intermediate structures occupy adjacent fields in the An–Ab series, and that the calcium-rich component of the peristerites cannot form a relatively large homogeneous crystal. It seems likely that the calcium-rich and soda-rich regions in the normally accepted model of the intermediate structure can be identified with body-centred anorthite (Sörum, 1951) and the calcium-rich component of the unmixed albite-oligoclases. For low-temperature materials the region of stable separate existence of body-centred anorthite is in doubt since it now appears that the transitional anorthite D pattern occurs for specimens more sodic than was suspected earlier. Traces of the diffuse type (*c*) reflections characteristic of the transitional anorthite structure have been found on intermediate patterns, suggesting that the intermediate and transitional anorthite structures may have a field of coexistence.

Further work is proceeding to elucidate the changes occurring at the boundaries of the intermediate structure and to establish the relationships between the two two-phase regions, together with an examination of very sodic specimens. Succeeding publications will describe the heat treatment of the intermediate plagioclases and the structural significance of the present work.

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# *The orientation of the pericline twin lamellae in triclinic alkali felspars.*

(With Plate II.)

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[Read 3 November 1955.]

*Summary.*—Cross-hatched twinning is characteristic of two alkali-felspar species, microclines and anorthoclases. Because of the difference in the crystallographic angles of these two species, the cross-hatched twinning is most clearly seen in (001) sections of microcline and in sections perpendicular to the *a* crystallographic axis in anorthoclases. If pericline twinning is present it is generally seen in (010) sections of microclines, but if the microcline is microperthitic the twin lamellae may not be seen. Strings or lamellae of perthitic albite can be distinguished from pericline twin lamellae by refractive index differences and also by the angle that their trace makes with the trace of (001) in (010) sections.

CROSS-HATCHED twinning is commonly seen both in microclines and in some sodium-rich alkali felspars, and because of the optical similarity between these two felspars many investigators have looked for a solid-solution series from microcline to albite. Recent studies of the alkali felspars have indicated that the complexly twinned sodium-rich felspars are high-temperature forms, whereas microcline is generally accepted to be a low-temperature form.[1] The observed sodium content of natural microclines is uniformly low (MacKenzie, 1954), so that the practical significance of a possible solid-solution series from microcline to albite is trifling. The purpose of this note is to draw attention to the difference between the twinning shown by microcline and that seen in some sodium-rich alkali felspars, of the type properly referred to as anorthoclase.[2]

[1] The term 'high-temperature' here implies that the felspar has been quickly cooled in a volcanic rock and so has retained the characteristics of its high-temperature origin. A low-temperature felspar may have crystallized at high temperature but on slow cooling inverted to a low-temperature form.

[2] The vague and imprecise usages of the name anorthoclase adopted by some writers obscure the value of the original definition of the word. The mineral name anorthoclase was first proposed by Rosenbusch (1885, p. 549) for certain *anorthic* sodium-rich alkali felspars multiply twinned after the albite and pericline laws, but

Anorthoclases are sometimes unmixed on a sub-microscopic scale, but usually they can be homogenized by heating at 900° C. for a few minutes. Cross-hatched twinning may be observed optically both in unmixed and homogeneous crystals.

Microclines are generally perthitic and are not readily rendered homogeneous. The lattice parameters of the potassium phase of a microcline-perthite may vary considerably (MacKenzie, 1952), and this variation is sometimes found even within a single small cleavage fragment. Specimens with the maximum deviation from monoclinic symmetry ($\alpha = 90° 41'$ and $\gamma = 87° 30'$) are very common and will be described as maximum microclines; those with less than the maximum deviation will be termed intermediate microclines.

Both microclines and anorthoclases are characterized by two sets of multiple twin lamellae which in certain orientations give the cross-hatched appearance in thin section. Laves (1950, 1952) established by X-ray methods that in the specimens he studied, both microclines and anorthoclases, the twin laws were albite and pericline. Other twin laws producing polysynthetic twin lamellae are possible in these felspars, but so far the writer has not observed multiple twinning based on any other laws. The albite twin law is defined as reflection across the (010) plane or as 180° rotation about an axis perpendicular to (010) and inversion through the centre. The composition plane is (010). The pericline twin law is 180° rotation about the *b*-axis, and the composition plane is an irrational plane that contains the *b*-axis and intersects the (010) plane in a line perpendicular to the *b*-axis. This plane is known as the rhombic section. The orientation of the rhombic section is sensitive to small changes in lattice angles, and some mineralogy textbooks give a method for determining the composition of plagioclase felspars from a measurement of the angle $\sigma$, which the trace of the pericline twin lamellae makes with the *a*-axis in (010) sections.

The angle $\sigma$ may be calculated from the relation $\cot \sigma = \cos(001) \wedge (010)/\cot \gamma$ (Story-Maskelyne, 1895; Lewis, 1899; Tunell, 1952). The sign of the angle $\sigma$ will be positive if measured from the positive direction of the *a*-axis towards the positive direction of the *c*-axis, and negative if

with a cleavage angle very close to 90°. From specimens known at that time Rosenbusch gave the limits of chemical composition of the anorthoclase series as $Or_{33}Ab_{67}$–$Or_{17}Ab_{83}$ with some anorthite in solid solution. From the work of Foerstner (1884), Rosenbusch knew that the anorthoclases when heated became optically monoclinic and reverted to anorthic symmetry even on rapid cooling. The name anorthoclase will be used here in essentially the same sense as proposed by Rosenbusch; but I hope to discuss this matter separately in another place.

measured from the negative direction of the $a$-axis, towards the positive direction of the $c$-axis.

TABLE I. The position of the rhombic section in triclinic alkali felspars, calculated from the relation $\cot \sigma = \cos(001) \wedge (010) / \cot \gamma$.

| | | (001) ∧ (010). | $\gamma$. | $\sigma$. |
|---|---|---|---|---|
| High-temperature albite and anorthoclases (synthetic) (Donnay and Donnay, 1952). | Ab | 85° 50′ | 90° 11′ | −2° 31′ |
| | $Or_{10}Ab_{90}$ | 86° 29′ | 90° 10′ | −2° 43′ |
| | $Or_{20}Ab_{80}$ | 87° 27′ | 90° 18′ | −6° 43′* |
| | $Or_{30}Ab_{70}$ | 88° 29′ | 90° 07′ | −4° 24′ |
| Microclines (MacKenzie, 1954). | Blue Mt., Ontario | 90° 18′ | 87° 31′ | −83° 07′ |
| | Spencer E† | 90° 09′ | 88° 48′ | −82° 53′ |
| | Spencer U† | 90° 05′ | 89° 11′ | −84° 11′ |

* This value appears to be high and is probably due to an error in the value of $\gamma$. Very slight errors in the determination of lattice angles produce a marked effect on the value of $\sigma$.

† Specimens described by Spencer (1937). The letters E and U were those given by Spencer to designate these specimens.

The angle $\sigma$ has been calculated for three anorthoclases and high-temperature albite from the lattice angles given by Donnay and Donnay (1952) and also for a maximum microcline and two intermediate microclines (MacKenzie, 1954). From the values given in table I it can be seen that the trace of the pericline twin lamellae makes a small angle with the trace of the (001) cleavage in the anorthoclases and high-temperature albite, whereas in microclines it is more nearly at right angles to the trace of the (001) cleavage. In both cases the variations in $\sigma$ are not sufficiently large to be useful in determining the departure of the lattices from monoclinic symmetry. Plate II, fig. 1A, is a photomicrograph of a thin section of a crystal of anorthoclase from a volcanic bomb from Camperdown, Victoria, Australia, cut perpendicular to the $a$-axis. The lamellae twinned according to the albite law are parallel to the long dimension of the photograph, and those twinned according to the pericline law are approximately at right angles. A section of the same crystal cut parallel to (010) is illustrated in fig. 1B, and here the $c$-axis is parallel to the long dimension of the photograph. The angle between the trace of the pericline twin lamellae and the trace of (001) measured from this photograph is about $-3\frac{1}{2}°$, a value which compares well with the calculated values for synthetic anorthoclases.[1]

Plate II, fig. 2A, shows an (001) cleavage section of a crystal of microcline from the Hugo mine, Black Hills, South Dakota. This felspar poikilitically encloses albite crystals but is almost entirely free from

[1] Rosenbusch (1885, p. 550) gives the value of $\sigma$ as 4–6° and, rarely, 8°.

microperthitic albite. The lamellae parallel to the long dimension of the photograph are twinned according to the albite law, and those approximately at right angles are twinned according to the pericline law. Fig. 2B is a section of the same crystal cut parallel to (010), and the *c*-axis is parallel to the long dimension of the photograph as in fig. 1B. The angle between the trace of the pericline lamellae and the trace of (001) in this photograph is about $-83°$, a value close to the calculated values for microclines. An exact value for the angle $\sigma$ cannot be measured since the traces of the composition planes of the pericline twin lamellae are not straight lines; variations of the lattice angles within this crystal undoubtedly account for the deviations from straight lines.

An (001) section of a microcline-perthite from the Diamond Match Company mine, Topsham, Maine, is illustrated in plate II, fig. 3A. Albite veins appear grey in the photograph, and the twin lamellae in the microcline, particularly those twinned on the pericline law, are much narrower and are clearly defined adjacent to the albite veins. A section of the same crystal cut parallel to (010) is shown in fig. 3B. Microperthitic albite strings, too small to be seen in fig. 3A, are oriented so that their trace makes an angle of $-107\frac{1}{2}°$ or $+72\frac{1}{2}°$ with the trace of (001) in the (010) plane. This value of $72\frac{1}{2}°$ for the acute angle is close to that generally given for the orientation of albite strings or lamellae in microcline- or orthoclase-microperthites (Bøggild, 1924; Andersen, 1928; Spencer, 1930), although other orientations have been reported (Bøggild, 1924; Spencer, 1930). The trace of the microperthitic strings in the (010) plane therefore makes an angle of about 25° with the trace of the rhombic section, but pericline twin lamellae, although clearly visible in the (001) section, can be seen only in a few places in this section and then only after very careful examination. Study of a number of microcline-microperthites reveals that when microperthitic albite strings are clearly seen in (010) sections the pericline twin lamellae are not readily visible and sometimes cannot be seen at all. Since microclines are commonly microperthitic it would appear that (010) sections would be extremely difficult to distinguish from (010) sections of orthoclase-microperthite in the absence of visible pericline twinning. Statements regarding the relative amounts of orthoclase and microcline in acid plutonic rocks should therefore be made only with the greatest caution, not only because microcline may be untwinned, but also because the twinning may not be readily observed in sections nearly parallel to (010).

One sodium-rich alkali felspar that cannot be classed as an anorthoclase has been found to have cross-hatched twinning. Tilley (1954)

described a felspar of composition $Or_{19\cdot8}Ab_{72\cdot7}An_{6\cdot0}Ce_{1\cdot5}$ from a nepheline-syenite in Mogok, Burma, as an orthoclase-cryptoperthite. Optical examination of a sample kindly provided by Professor C. E. Tilley revealed that, although most of the crystals were optically monoclinic, one or two had cross-hatched twinning. X-ray study revealed that the sodium felspar phase was similar to low-temperature albite in lattice angles, and heating at 1050° C. for 65 hours was not sufficient to homogenize completely the two phases (MacKenzie and Smith, 1955). The specimen probably crystallized as a homogeneous anorthoclase, unmixed to an anorthoclase-cryptoperthite with a sodium felspar phase of high-temperature albite, and finally, when the sodium-rich phase inverted to low-temperature albite, reached its present state. This felspar is best described as an orthoclase-cryptoperthite or orthoclase-microperthite, indicating that it has a low-temperature sodium felspar phase (MacKenzie and Smith, 1955).

To summarize, cross-hatched twinning is characteristic of two alkali felspar species, namely microclines and anorthoclases. Because of the difference in the crystallographic angles of these two species, the cross-hatched twinning is most clearly seen in (001) sections of microcline and in sections perpendicular to the *a* crystallographic axis in anorthoclase. If pericline twinning is present it is generally seen in (010) sections of microclines, but if the microcline is microperthitic the twin lamellae may not be seen. Strings or lamellae of perthitic albite can be distinguished from pericline twin lamellae by refractive index differences and also by the angle which their trace makes with the trace of (001) in (010) sections.

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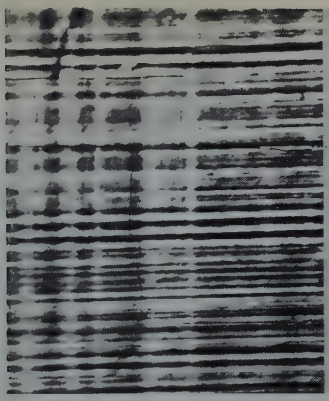
Plate II.

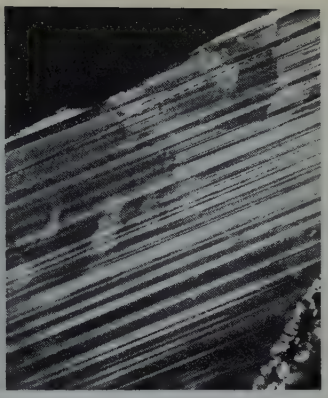
Fig. 1. Photomicrographs of thin sections of anorthoclase from a volcanic bomb, Camperdown, Victoria, Australia. A. Section perpendicular to the *a*-axis showing albite and pericline twinning. Crossed nicols; ×60. B. Section parallel to (010) showing pericline twin lamellae whose trace is inclined to that of the (001) cleavage at $-3\frac{1}{2}^\circ$. Crossed nicols; ×50. The trace of the (001) cleavage is marked by a broken line since it does not show clearly in the photograph.

Fig. 2. Photomicrographs of thin sections of microcline from Hugo mine, Black Hills, South Dakota. A. Section parallel to (001) showing albite and pericline twinning. Crossed nicols; ×50. B. Section parallel to (010). The traces of the pericline twin lamellae do not form straight lines but make an angle of approximately 83° with the trace of the (001) cleavage. Crossed nicols; ×200.

Fig. 3. Photomicrographs of thin sections of microcline-perthite from the Diamond Match Company mine, Topsham, Maine. A. Section parallel to (001). Veins of perthitic albite appear grey in the photograph, and adjacent to these veins the pericline twin lamellae in the microcline are much narrower and more clearly defined than elsewhere in the section. Crossed nicols; ×50. B. Section parallel to (010). Strings of microperthitic albite lie at $72\frac{1}{2}^\circ$ to the trace of the (001) cleavage. Crossed nicols; ×200.



1A



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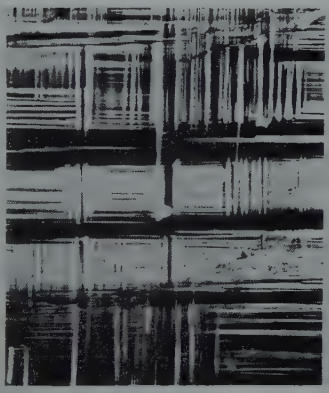
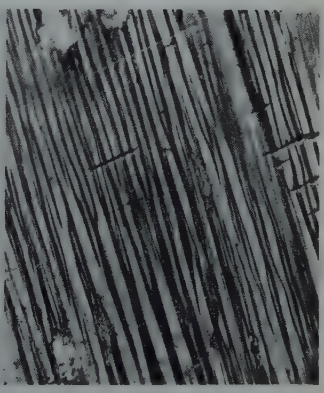
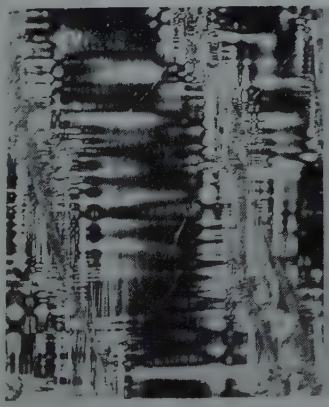


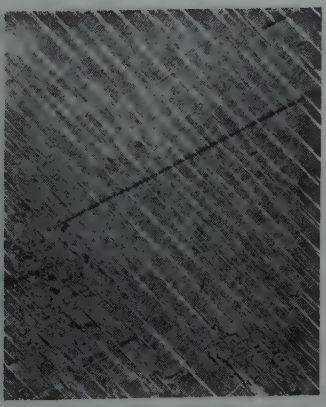
2A



2B



3A



3B

W. S. MACKENZIE: PERICLINE TWINNING

# *The powder patterns and lattice parameters of plagioclase felspars. I. The soda-rich plagioclases.*

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[Read 24 March 1955.]

*Summary.*—Geiger-counter powder records of soda-rich plagioclases have been carefully measured and indexed. The lattice parameters of the synthetic specimens are almost independent of the lime content, the largest variation (that in $\beta^*$) amounting to only 0·2°. After strong heating the powder patterns of the natural specimens closely approached those of the synthetic specimens.

Eight out of the nine natural plagioclases gave lattice parameters which fall within experimental error on a continuous line. There is a fairly large variation in lattice parameters, especially for $\gamma^*$, which changes by 2°. As the lime content increases the lattice parameters of the natural plagioclases approach those for the high-temperature synthetic and heated natural specimens until at $An_{50}$ the separation is only one-fifth of that at $An_0$. The ninth specimen (from a dacite) gives parameters midway between the curves, thus exhibiting a state of partial inversion.

The partially heated natural plagioclases and the plagioclase from the dacite give parameters indistinguishable within experimental error from the parameters of unheated plagioclases with a higher lime content. There is, therefore, no reliable powder X-ray method for the determination of composition in the region $An_0$–$An_{50}$. If the composition is known the powder method may be used for the determination of the thermal state. If the plagioclase can be judged to be in the low-temperature state from geological evidence the powder method can be used to estimate the composition with an accuracy of 2 % An.

RESEARCH carried out by many workers in the last few decades culminated in the conclusive demonstration by Tuttle and Bowen (1950) that there are two structural series of soda-rich plagioclases. Careful measurements of the optic axial angle, 2V, and of the difference between the Bragg angles $2\theta(1\bar{3}2)$[2] and $2\theta(1\bar{3}1)$ showed that natural soda-rich plagioclases from low-temperature[3] environments differed

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[2] The detailed measurements made in the present work show that this is the (131) reflection. Throughout the remainder of the paper the correction will be made without further reference.

[3] A low-temperature environment is taken to be one for which there has been ample opportunity for attainment of the state which is stable at low temperatures. This definition includes plutonic conditions.

considerably from their synthetic counterparts but could be converted into a similar state by prolonged heating just below the solidus. A natural plagioclase from a high-temperature environment, rhyolite, gave results close to those for the synthetic material. Tuttle and Bowen found that the differences between the two series decreased as the proportion of lime increased from $An_0$ to $An_{50}$, at which composition the differences were slight.

As plagioclase felspars are anorthic and have six independent lattice parameters, the author hoped that detailed examination of accurate X-ray powder patterns would lead to a routine X-ray method for the determination of the two variables, composition and thermal state. In addition, careful measurements might yield information on the position of the boundaries between regions of different structure. In view of the successful use by Donnay and Donnay (1952) of the Geiger-counter focusing-diffractometer in the study of high-temperature alkali felspars, this method was chosen in preference to the less accurate photographic powder method and the more tedious single-crystal method. The powerful resolution and high accuracy at low angles of the focusing-diffractometer permit the indexing of powder patterns and the determination of the lattice parameters for anorthic crystals.

Three studies of the powder patterns of plagioclase felspars have so far been recorded. Claisse (1950) published photographic powder patterns of eight natural plagioclases together with determinative curves based on the positions of certain reflections on the photographic film. The effect of thermal state was not considered. Chayes and Robbins (1953) have measured certain angular relations from diffractometer records of albites and oligoclases. Goodyear and Duffin (1954) have recently examined the powder patterns of sixteen natural and ten synthetic specimens by photographic methods, with the following two objects:

(i) to provide X-ray powder data for the identification of plagioclase felspars when admixed with associated minerals, and (ii) to establish relationships enabling the composition and thermal modification of a felspar to be determined from certain line positions in the X-ray pattern.

Studies of soda-rich plagioclases by single-crystal techniques have been reported by Cole, Sörum, and Taylor (1951), Laves (1954), Gay and Smith (1955), and Gay (1956). Laves found that some natural albites and oligoclases are unmixed into two phases of composition near $An_0$ and $An_{50}$ (known as unmixing of the peristerite type). This unmixing was confirmed by Gay and Smith, who found that the lattice angles $\alpha^*$ and $\gamma^*$ of the two phases corresponded to compositions near $An_3$ and

$An_{23}$. Cole *et al.* found that in the region $An_{30}$–$An_{70}$ the X-ray rotation patterns showed weak subsidiary layer-lines in addition to the strong layer-lines which correspond to the 7 Å. albite-type structure. More detailed study by Gay has revealed that most natural specimens in the composition range $An_{20}$–$An_{70}$ exhibit these subsidiary layer-lines. Certain specimens from high-temperature environments revealed either no subsidiary layer-lines or very weak diffuse ones. None of the powder records obtained in the present study has shown the presence of the subsidiary reflections: this is not surprising, for measurements made on the single-crystal cameras showed that their intensities are small.

Two of the specimens used in the present investigation of the lattice parameters lie in the range $An_3$–$An_{20}$ for which unmixing of the peristerite type might be expected. Single-crystal photographs of specimen 81822, composition $An_{17·9}$, reveal no unmixing, in contrast to photographs of the other specimen, BM 1940,27, composition $An_{11·2}$, which do. The powder record of the latter specimen, however, does not give a clear

TABLE I. Origin and chemical composition of the plagioclase samples.

| Label number. | Origin. | Ref. | Weight % An. | Ab. | Or. | 100 An/(An+Ab) |
|---|---|---|---|---|---|---|
| Amelia | Amelia, Va., pegmatite. | 1 | 0·0 | 98·2 | 1·8 | 0·0 |
| BM 1940,27 | Kenya, pegmatite. | 2 | 10·9 | 86·5 | 2·6 | 11·2 |
| 81822 | South Carolina, pegmatite. | 1 | 17·7 | 81·0 | 1·3 | 17·9 |
| 103086 | Hawk Mine, N.C., pegmatite. | 1 | 22·1 | 74·4 | 3·5 | 22·9 |
| 97490 | Little Rock Creek, Mitchel Co., N.C., pegmatite. | 1 | 29·9 | 66·5 | 3·6 | 31·0 |
| 152 (6) | Spanish Peak, Calif., gneissoid granodiorite. | 3 | 35·9 | 62·6 | 1·5 | 36·4 |
| 64 (7) | San Luis Obispo Co., Calif., dacite. | 3 | 36·1 | 60·7 | 3·2 | 37·3 |
| 144 (8) | Crestmore, Calif., granodiorite. | 3 | 38·0 | 60·0 | 2·0 | 38·8 |
| 24 (9) | Essex Co., N.Y., anorthosite. | 3 | 49·0 | 47·2 | 3·8 | 50·9 |
| | Synthetic; 5 days 800° C. and 1000 Kg./cm.$^2$ $H_2O$. | 4 | 0·0 | 100·0 | 0·0 | 0·0 |
| | Synthetic; 70 days 1080° C.; 90 days 1100° C.; dry. | 5 | 10·0 | 90·0 | 0·0 | 10·0 |
| | Synthetic; 26 days 1150° C., 14 days 1140° C.; dry. | 5 | 30·0 | 70·0 | 0·0 | 30·0 |
| | Synthetic; dry. | 5 | 40·0 | 60·0 | 0·0 | 40·0 |
| | Synthetic; 5 days 1230° C., 11 days 1170° C.; dry. | 5 | 50·0 | 50·0 | 0·0 | 50·0 |

1. Kracek and Neuvonen (1952).
2. Game (1949).
3. Emmons *et al.* (1953).
4. Bowen and Tuttle (1950).
5. J. F. Schairer, unpublished.

indication of the presence of two phases and may be indexed on the basis of a single phase. Examination of powder records of several other specimens in this composition range (listed in table VII) also reveals the difficulty of detecting unmixing. Only when the proportions of the two phases are roughly equal can the unmixing be detected with certainty in powder records of peristerites. It is doubtful if the lower resolution of the photographic powder methods permits the detection of peristeritic unmixing even when the proportions are nearly equal. Although the unmixing is not obvious in the records of BM 1940,27 it is likely that the lattice parameters deduced on the basis of a single phase do not give a true average of the two phases: but the error is probably no larger than the effect produced by 2 % An. Precautions for minimizing this error are given in the final section of this paper.

TABLE II. Indexed powder patterns of Amelia albite. Cu-$K\alpha$ radiation. Only those reflections with $2\theta_{calc}$ sufficiently close to observed values of $2\theta$ to make a contribution possible are listed. The observed values of $2\theta$ are the means of four observations.

| Natural Amelia albite. | | | | Heated Amelia albite. | | | |
|---|---|---|---|---|---|---|---|
| *I.* | $2\theta$obs. | $2\theta$calc. | (*hkl*). | *I.* | $2\theta$obs. | $2\theta$calc. | (*hkl*). |
| 75 | 13·86 | 13·855 | 001 | — | — | 13·73 | $1\bar{1}0$ |
| — | — | 13·89 | 020 | 20 | 13·775 | 13·79 | 020 |
| 2 | 14·9 | 14·98 | $11\bar{1}$ | 30 | 13·93 | 13·94 | 001 |
| 4 | 15·85 | 15·86 | $\bar{1}11$ | 3 | 15·17 | 15·185 | $11\bar{1}$ |
| 60 | 22·057 | 22·055 | $20\bar{1}$ | 3 | 15·64 | 15·68 | $\bar{1}11$ |
| 20 | 23·071 | 23·07 | $1\bar{1}1$ | 2 | 18·92 | 18·955 | $02\bar{1}$ |
| 85 | 23·538 | 23·54 | 111 | 60 | 22·00 | 21·995 | $20\bar{1}$ |
| 70 | 24·155 | 24·155 | 130 | 40 | 22·915 | 22·905 | $1\bar{1}1$ |
| 50 | 24·306 | 24·27 | $13\bar{1}$ | 100 | 23·73 | 23·715 | $1\bar{3}0$ |
| — | — | 24·335 | $1\bar{3}0$ | — | — | 23·75 | 111 |
| 5 | 25·185 | — | 002$\beta$ | 35 | 24·46 | 24·47 | 130 |
| 35 | 25·392 | 25·40 | $11\bar{2}$ | — | — | 24·54 | $13\bar{1}$ |
| 5 | 25·57 | 25·565 | $22\bar{1}$ | 5 | 25·35 | — | 002$\beta$ |
| 20 | 26·418 | 26·415 | $\bar{1}12$ | 15 | 25·63 | 25·635 | $11\bar{2}$ |
| 360 | 27·915 | 27·92 | 002 | 25 | 26·445 | 26·46 | $\bar{1}12$ |
| — | — | 27·99 | 040 | — | — | 27·66 | $2\bar{2}0$ |
| — | — | 28·12 | 220 | 160 | 27·785 | 27·79 | 040 |
| 30 | 28·325 | 28·325 | $2\bar{2}0$ | — | — | 27·805 | $20\bar{2}$ |
| 30 | 30·148 | 30·145 | $1\bar{3}1$ | 360 | 28·095 | 28·095 | 002 |
| — | — | 30·225 | $22\bar{2}$ | 40 | 28·525 | 28·535 | 220 |
| 50 | 30·48 | 30·51 | $02\bar{2}$ | 25 | 29·62 | 29·62 | $1\bar{3}1$ |
| — | — | 30·54 | $04\bar{1}$ | 30 | 30·295 | 30·305 | $04\bar{1}$ |
| 20 | 31·210 | 31·23 | 131 | 35 | 30·54 | 30·52 | $02\bar{2}$ |
| 3 | 31·47 | 31·505 | $13\bar{2}$ | 5? | 30·65 | 30·655 | $22\bar{2}$ |
| 3 | 32·11 | 32·105 | 022 | 35 | 31·61 | 31·595 | 131 |
| $\alpha_1$ | | | | $\alpha_1$ | | | |
| — | — | 32·155 | 041 | 12 | 33·74 | 33·745 | $\bar{1}32$ |
| 15 | 33·946 | 33·94 | $\bar{1}32$ | — | — | 33·78 | $31\bar{1}$ |

TABLE II (*cont.*)

| Natural Amelia albite. | | | | Heated Amelia albite. | | | |
|---|---|---|---|---|---|---|---|
| *I.* | 2θobs. | 2θcalc. | (*hkl*). | *I.* | 2θobs. | 2θcalc. | (*hkl*). |
| 20 | 34·996 | 34·995 | $24\bar{1}$ | — | — | 35·57 | $31\bar{2}$ |
| 3 | 35·34 | 35·32 | $31\bar{2}$ | 20 | 35·62 | 35·595 | $24\bar{1}$ |
| 4 | 35·72 | 35·70 | $1\bar{1}2$ | | | 35·685 | $1\bar{1}2$ |
| 2 | 35·95 | 35·945 | $2\bar{2}1$ | 20 | 35·80 | 35·78 | $\bar{2}41$ |
| 2 | 36·5 | 36·495 | 221 | — | — | 35·835 | $\bar{3}12$ |
| 7 | 36·757 | 36·76 | $\bar{2}41$ | 3 | 36·655 | 36·64 | 112 |
| 5 | 36·95 | 36·955 | $15\bar{1}$ | — | — | 36·645 | $1\bar{5}0$ |
| 5 | 37·35 | 37·305 | 240 | 7 | 37·94 | 37·925 | 240 |
| — | — | 37·425 | $1\bar{5}0$ | 5 | 39·12 | 39·085 | $\bar{3}31$ |
| 7 | 37·64 | 37·625 | 310 | 4 | 39·47 | 39·44 | $33\bar{1}$ |
| 10 | 38·78 | 38·78 | $33\bar{1}$ | 5 | 39·735 | 39·72 | $\bar{1}13$ |
| 4 | 39·52 | 39·515 | $\bar{1}13$ | 3 | 40·13 | 40·13 | $1\bar{3}2$ |
| 10 | 41·21 | 41·20 | 042 | — | 40·49 | 40·485 | $\bar{2}42$ |
| — | — | 41·22 | $\bar{2}42$ | — | — | 40·515 | $1\bar{5}1$ |
| 20 | 42·51 | 42·50 | 060 | 2 | 41·34 | 41·32 | 042 |
| — | — | 42·62 | $13\bar{3}$ | — | — | 41·375 | $\bar{3}32$ |
| 15 | 42·63 | 42·665 | 151 | 20 | 42·19 | 42·19 | 060 |
| 5 | 43·55 | 43·545 | $24\bar{1}$ | — | — | 42·535 | $31\bar{3}$ |
| 5 | 44·48 | 44·47 | 241 | 15 | 42·6 | 42·665 | 003 |
| 3 | 45·29 | 45·305 | 202 | — | — | 42·70 | 132 |
| 10 | 45·78 | 45·795 | 061 | 7 | 43·025 | 43·025 | 151 |
| 5 | 47·125 | 47·145 | $42\bar{1}$ | 3? | 45·5 | 45·47 | $\bar{1}13$ |
| — | — | 48·105 | $35\bar{1}$ | 5 | 45·62 | 45·605 | $3\bar{1}1$ |
| 20 | 48·115 | 48·11 | 222 | — | — | 46·735 | $24\bar{3}$ |
| 8 | 49·17 | 49·19 | $40\bar{3}$ | 5 | 46·77 | 46·755 | $2\bar{2}2$ |
| 10 | 49·38 | 49·405 | $1\bar{5}2$ | 3 | 47·2 | 47·19 | $\bar{4}22$ |
| — | — | 49·405 | $\bar{2}61$ | 15 | 48·57 | 48·57 | 222 |
| — | — | 49·435 | 260 | 5 | 49·22 | 49·175 | $40\bar{3}$ |
| 15 | 49·80 | 49·82 | $2\bar{6}0$ | — | — | 49·875 | $04\bar{3}$ |
| — | — | 49·825 | $\bar{2}43$ | 20 | 49·89 | 49·88 | $1\bar{1}3$ |
| 65 | 49·945 | 49·93 | $04\bar{3}$ | | — | 49·88 | 400 |
| — | — | 49·98 | $35\bar{1}$ | 5 | 50·1 | 50·11 | 260 |
| — | — | 49·985 | $06\bar{2}$ | 35 | 50·91 | 50·915 | 113 |
| 20 | 50·54 | 50·55 | 113 | 25 | 51·46 | 51·455 | $20\bar{4}$ |
| 30 | 51·115 | 51·12 | $20\bar{4}$ | — | — | — | — |

Seven out of the nine natural plagioclases used in the determination of lattice parameters were converted into the high-temperature form by prolonged heating just under the solidus. A large sample was put into a furnace and heated for several days. A small amount was removed and a powder record obtained. The remainder was reheated. This cycle was continued until no further change occurred in the X-ray pattern, when it was assumed that the material was in the high-temperature form. Lack of material prevented the complete conversion of specimen BM 1940,27.

TABLE III. $2\theta$ values for the soda-rich plagioclases.

| Indices. | $20\bar{1}$. | $1\bar{1}1$. | 111. | $1\bar{3}0$. | 130. | $11\bar{2}$. | $\bar{1}12$. | 040. | 002. | 220. | $1\bar{3}1$. | 131. | $\bar{1}32$. | $24\bar{1}$. | $\bar{2}41$. | 060. | 222. | 113. | $20\bar{4}$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | $\alpha_1+\alpha_2$ | | $\alpha_1$ only | | | | | | |
| *Unheated* | | | | | | | | | | | | | | | | | | | |
| Amelia... ... ... | 22·057 | 23·071 | 23·538 | 24·306 | 24·155 | 25·392 | 26·418 | – | — | — | 30·148 | 31·210 | 33·946 | 34·996 | 36·757 | 42·507 | 48·118 | 50·548 | 51·118 |
| BM 1940,27 ... ... | 22·042 | 23·03 | 23·567 | 24·19 | 24·19 | 25·445 | 26·427 | – | — | — | 30·04 | 31·295 | 33·908 | 35·108 | 36·557 | 42·425 | 48·193 | 50·614 | 51·168 |
| 81822 ... ... ... | 22·013 | 22·981 | 23·586 | 24·078 | 24·248 | 25·486 | 26·428 | — | — | — | 29·941 | 31·346 | 33·876 | 35·202 | 36·42 | 42·363 | 48·235 | 50·666 | 51·273 |
| 103086 ... ... | 22·00 | 22·958 | 23·60 | 23·988 | 24·275 | 25·508 | 26·435 | — | — | – | 29·838 | 31·363 | 33·833 | 35·270 | 36·223 | 42·31 | 48·245 | 50·69 | 51·288 |
| 97490 ... ... ... | 21·983 | 22·918 | 23·612 | 23·922 | 24·302 | 25·542 | 26·435 | – | — | — | 29·782 | 31·377 | 33·799 | 35·319 | 36·125 | 42·285 | 48·32 | 50·722 | 51·337 |
| 152 ... ... ... | 22·01 | 22·925 | 23·655 | 23·88 | 24·36 | 25·565 | 26·458 | 27·84 | 28·032 | 28·365 | 29·73 | 31·465 | 33·815 | 35·43 | 36·065 | 42·275 | 48·385 | 50·765 | 51·40 |
| 64 ... ... ... | 21·99 | 22·865 | — | — | 24·39 | 25·625 | 26·455 | 27·80 | 28·04 | 28·44 | 29·65 | 31·49 | 33·76 | — | — | 42·22 | 48·42 | 50·79 | 51·455 |
| 144 ... ... ... | 22·015 | 22·895 | — | — | 24·375 | 25·575 | 26·45 | 27·815 | 28·035 | 28·37 | 29·71 | 31·46 | 33·81 | — | — | 42·24 | 48·37 | 50·77 | 51·415 |
| 24 ... ... ... | 21·967 | 22·862 | — | — | 24·369 | 25·644 | 26·435 | 27·80 | 28·037 | 28·374 | 29·649 | 31·462 | 33·772 | — | — | 42·235 | 48·354 | 50·752 | 51·452 |
| *Heated* | | | | | | | | | | | | | | | | | | | |
| Amelia... ... ... | 22·00 | 22·915 | — | — | 24·46 | 25·63 | 26·445 | 27·785 | 28·095 | 28·525 | 29·62 | 31·61 | 33·74 | — | — | 42·19 | 48·57 | 50·91 | 51·46 |
| BM 1940,27; 12 days | 22·02 | 22·97 | — | — | 24·33 | 25·52 | 26·42 | 27·84 | 28·005 | 28·315 | 29·81 | 31·435 | 33·82 | — | — | 42·305 | 48·40 | 50·73 | 51·33 |
| BM 1940,27; 24 days | 22·012 | 22·92 | — | — | 24·397 | 25·57 | 26·435 | 27·827 | 28·047 | 28·44 | 29·665 | 31·47 | 33·76 | — | — | 42·225 | 48·49 | 50·835 | 51·385 |
| 81822 ... ... ... | 21·998 | 22·863 | — | — | 24·44 | 25·61 | 26·44 | 27·773 | 28·053 | 28·483 | 29·60 | 31·54 | 33·735 | — | – | 42·18 | 48·49 | 50·85 | 51·45 |
| 103086 ... ... | 21·985 | 22·88 | — | — | 24·435 | 25·60 | 26·42 | 27·75 | 28·04 | 28·47 | 29·59 | 31·52 | 33·66 | — | — | 42·15 | 48·46 | 50·81 | 51·43 |
| 97490 ... ... ... | 21·99 | 22·855 | — | – | 24·427 | 25·652 | 26·45 | 27·775 | 28·045 | 28·465 | 29·58 | 31·492 | 33·69 | | — | 42·16 | 48·425 | 50·79 | 51·435 |
| 152 ... ... ... | 21·988 | 22·868 | — | — | 24·460 | 25·655 | 26·47 | 27·797 | 28·057 | 28·477 | 29·587 | 31·535 | 33·75 | — | — | 42·18 | 48·46 | 50·828 | 51·463 |
| 64 ... ... ... | 21·988 | 22·848 | — | — | 24·435 | 25·625 | 26·455 | 27·782 | 28·027 | 28·442 | 29·562 | 31·525 | 33·72 | — | — | 42·185 | 48·47 | 50·793 | 51·453 |
| *Synthetic* | | | | | | | | | | | | | | | | | | | |
| $An_0$ ... ... ... | 22·005 | 22·885 | – | — | 24·465 | 25·65 | 26·48 | 27·80 | 28·085 | 28·53 | 29·59 | 31·62 | 33·75 | — | – | 42·19 | 48·54 | 50·92 | 51·475 |
| $An_{10}$ ... ... ... | 22·025 | 22·875 | — | — | 24·475 | 25·66 | 26·47 | 27·805 | 28·075 | 28·53 | 29·605 | 31·585 | 33·735 | — | — | 42·19 | 48·56 | 50·91 | 51·47 |
| $An_{30}$ ... ... ... | 22·025 | 22·855 | — | – | 24·455 | 25·67 | 26·43 | 27·795 | 28·04 | 28·485 | 29·59 | 31·52 | 33·735 | – | — | 42·18 | 48·475 | 50·83 | 51·48 |
| $An_{50}$ ... ... ... | 22·02 | 22·805 | — | — | 24·47 | 25·675 | 26·46 | 27·81 | 28·03 | 28·46 | 29·55 | 31·525 | 33·735 | — | — | 42·195 | 48·395 | 50·815 | 51·515 |

*Experimental procedure for the determination of the lattice parameters.*

X-ray powder records were taken on a Norelco high-angle diffractometer using either pressed mounts made by the method of Adams and Rowe (1954) or carefully made smear mounts. The pressed mounts gave slightly more intense peaks than the smear mounts, but their preparation was more tedious and required more material. The settings of the diffractometer were: time constant, 4 seconds; divergence and scatter slits, 1°; receiving slit, 0·006 inches; scanning speed, 0·25 degree of $2\theta$ per minute; chart scale, one degree per inch; filtered Cu-$K\alpha$ radiation.

Measurements of the plagioclase peaks obtained from both types of mount agreed within random experimental error only when the records were calibrated from the peaks given by the secondary standard, quartz, which was intermixed with the plagioclase in the mount. The quartz sample is number F2-16 (Tuttle and Keith, 1952) and the positions of the quartz reflections were taken to be those listed by Parrish (1953).

The measurements on the synthetic albite disagreed with those given by Donnay and Donnay (1952) who used the same sample and the same instrumental setting except for the width of the receiving slit, which was half that used here. The corrected values of $2\theta$ were, on the average, about 0·025° higher than those given by Donnay and Donnay. In view of this discrepancy further measurements using both pressed and smear mounts were taken, but the discrepancy persisted. As the quartz and plagioclase were ground together in acetone for 5 minutes it seems certain that a homogeneous mixture was obtained and that the correction *relative to quartz* was valid. Donnay and Donnay calibrated the diffractometer by using a separate pressed mount of the secondary standard, silicon. There appear to be two possible explanations of the discrepancy: either the lattice parameters of quartz and silicon given by Parrish are not applicable to the samples used here, or the indirect method of calibration used by Donnay and Donnay was in error. In order to test the two explanations, photographic powder patterns of the silicon and the quartz were taken and measured according to the extrapolation procedure given by Nelson and Riley (1945), with the following results:

The lattice parameter of the silicon agrees within the experimental error of 1/20 000 with the value listed by Parrish and thence used by Donnay and Donnay.

The relative positions of the reflections of quartz and silicon obtained from a mixed powder specimen agree very closely with the values given by Parrish. Assuming the $2\theta$-values for the silicon (533) reflection to be identical with those given by Parrish, the adjacent quartz reflections $(14\bar{5}3)$ and $(20\bar{2}6)$ near $2\theta = 137°$ are 0·02° in $2\theta$ lower than those given by Parrish. Tuttle and Keith, however, found that for this particular quartz sample, F2-16, the $(23\bar{5}4)$ quartz reflection near $2\theta = 154°$ was 0·02° in $2\theta$ higher than the value given by Parrish. The discrepancy of 0·02° in $2\theta$ at these high angles corresponds to a discrepancy of about 1/15 000 in the lattice parameters and to 0·002° in $2\theta$ for $2\theta \approx 30°$.

From these measurements it seems reasonably certain that the positions of the quartz reflections assumed in the present work are accurate to about 1/15 000 and that an error in the indirect calibration method of Donnay and Donnay is the source of the discrepancy.

TABLE IV. Lattice parameters for soda-rich plagioclases.

| Sample. | Heating conditions. | Wt. % An / An+Ab | $a$ Å. | $b$ Å. | $c$ Å. | $\alpha$ degrees. | $\beta$ degrees. | $\gamma$ degrees. | $a^*$ Å.$^{-1}$ | $b^*$ Å.$^{-1}$ | $c^*$ Å.$^{-1}$ | $\alpha^*$ degrees. | $\beta^*$ degrees. | $\gamma^*$ degrees. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Amelia | natural | 0·0 | 8·144 | 12·787 | 7·160 | 94·26 | 116·58 | 87·67 | 0·1373 | 0·07843 | 0·15648 | 86·40 | 63·51 | 90·48 |
| BM 1940,27 | natural | 11·2 | 8·149 | 12·806 | 7·153 | 94·12 | 116·56 | 88·17 | 0·1372 | 0·07829 | 0·15662 | 86·31 | 63·50 | 89·99 |
| 81822 | natural | 17·9 | 8·152 | 12·821 | 7·139 | 93·99 | 116·46 | 88·58 | 0·1370 | 0·07819 | 0·15681 | 86·25 | 63·57 | 89·60 |
| 103086 | natural | 22·9 | 8·169 | 12·836 | 7·134 | 93·83 | 116·45 | 88·99 | 0·1367 | 0·07809 | 0·15688 | 86·23 | 63·56 | 89·22 |
| 97490 | natural | 31·0 | 8·171 | 12·846 | 7·129 | 93·75 | 116·44 | 89·25 | 0·1367 | 0·07803 | 0·15700 | 86·19 | 63·55 | 88·97 |
| 152 | natural | 36·4 | 8·160 | 12·848 | 7·121 | 93·72 | 116·36 | 89·52 | 0·1368 | 0·07802 | 0·15710 | 86·09 | 63·61 | 88·69 |
| 64 | natural | 37·3 | 8·166 | 12·864 | 7·112 | 93·51 | 116·30 | 89·98 | 0·1366 | 0·07792 | 0·15721 | 86·10 | 63·65 | 88·28 |
| 144 | natural | 38·8 | 8·164 | 12·857 | 7·118 | 93·69 | 116·34 | 89·59 | 0·1367 | 0·07796 | 0·15712 | 86·08 | 63·63 | 88·63 |
| 24 | natural | 50·9 | 8·180 | 12·859 | 7·112 | 93·52 | 116·27 | 89·89 | 0·1364 | 0·07794 | 0·15717 | 86·12 | 63·68 | 88·38 |
| Amelia | 23 days, 1060° C. | 0·0 | 8·165 | 12·872 | 7·111 | 93·45 | 116·43 | 90·28 | 0·1368 | 0·07788 | 0·15743 | 86·01 | 63·50 | 87·97 |
| BM 1940,27 | 12 days, 1060° C. | 11·2 | 8·157 | 12·841 | 7·131 | 93·83 | 116·45 | 89·24 | 0·1369 | 0·07806 | 0·15698 | 86·10 | 63·54 | 88·94 |
| BM 1940,27 | 24 days, 1060° C. | 11·2 | 8·167 | 12·864 | 7·122 | 93·62 | 116·44 | 89·87 | 0·1368 | 0·07792 | 0·15720 | 86·03 | 63·51 | 88·35 |
| 81822 | 42 days, 1090° C. | 17·9 | 8·169 | 12·877 | 7·112 | 93·48 | 116·35 | 90·20 | 0·1367 | 0·07785 | 0·15729 | 86·02 | 63·58 | 88·05 |
| 103086 | 42 days, 1090° C. | 22·9 | 8·175 | 12·884 | 7·115 | 93·40 | 116·36 | 90·24 | 0·1366 | 0·07780 | 0·15723 | 86·08 | 63·57 | 88·04 |
| 97490 | 42 days, 1090° C. | 31·0 | 8·174 | 12·880 | 7·112 | 93·34 | 116·30 | 90·29 | 0·1365 | 0·07782 | 0·15719 | 86·13 | 63·64 | 88·02 |
| 152 | 28 days, 1090° C. | 36·4 | 8·169 | 12·874 | 7·109 | 93·46 | 116·29 | 90·23 | 0·1366 | 0·07787 | 0·15727 | 86·02 | 63·64 | 88·03 |
| 64 | 14 days, 1090° C. | 37·3 | 8·172 | 12·876 | 7·112 | 93·44 | 116·29 | 90·28 | 0·1366 | 0·07785 | 0·15720 | 86·03 | 63·64 | 87·99 |
| $An_0$ | hydrothermal | 0·0 | 8·171 | 12·872 | 7·108 | 93·47 | 116·39 | 90·33 | 0·1367 | 0·07788 | 0·15743 | 85·96 | 63·53 | 87·90 |
| $An_{10}$ | dry, synthetic | 10·0 | 8·160 | 12·872 | 7·109 | 93·52 | 116·37 | 90·24 | 0·1369 | 0·07788 | 0·15740 | 85·95 | 63·56 | 87·99 |
| $An_{30}$ | dry, synthetic | 30·0 | 8·163 | 12·875 | 7·107 | 93·39 | 116·27 | 90·29 | 0·1367 | 0·07786 | 0·15728 | 86·07 | 63·66 | 88·00 |
| $An_{50}$ | dry, synthetic | 50·0 | 8·178 | 12·870 | 7·102 | 93·36 | 116·18 | 90·40 | 0·1363 | 0·07789 | 0·15727 | 86·06 | 63·74 | 87·90 |
| *Lattice parameter measurements recorded in the literature.* | | | | | | | | | | | | | | |
| Kodarma† | natural | ~ 0 | 8·135 | 12·788 | 7·154 | 94·23 | 116·52 | 87·71 | 0·1374 | 0·07841 | 0·15652 | 86·42 | 63·57 | 90·43 |
| 24† | natural | 50·9 | — | — | — | — | — | — | 0·1365 | 0·07792 | 0·15711 | 86·21 | — | 88·43 |
| Amelia‡ | natural | ~ 0 | 8·156 | 12·773 | 7·170 | 94·32 | 116·67 | 87·62 | 0·1370 | 0·07852 | 0·15635 | 86·37 | 63·43 | 90·50 |
| Amelia‡ | heated | ~ 0 | 8·115 | 12·871 | 7·127 | 93·57 | 116·50 | 89·98 | 0·1371 | 0·07798 | 0·15713 | 86·03 | 63·45 | 88·25 |
| $An_0$§ | hydrothermal | 0·0 | 8·172 | 12·884 | 7·123 | 93·65 | 116·45 | 90·19 | 0·1368 | 0·07782 | 0·15721 | 85·83 | 63·48 | 87·97 |

† Cole, Sörum, and Taylor (1951). ‡ Laves (1952). § Donnay and Donnay (1952).

The values of $2\theta$ for the plagioclase reflections, corrected by the quartz internal standard, were converted into Q-values by the tables of Donnay and Donnay (1951). The peaks were indexed with the aid of the accurate data given by Cole *et al.* (1951) and Donnay and Donnay (1952). Table II contains the data for the indexed patterns of low- and high-temperature albite. All other powder patterns obtained from soda-rich plagioclases may be indexed by interpolation, though some caution is necessary, especially for ($hk0$) and ($h\bar{k}0$) reflections, which interchange position as $\gamma^*$ passes through 90°.

The relation between Q and the reciprocal lattice parameters is given by the equation

$$Q_{(hkl)} = 1/d^2_{(hkl)} = h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2kl\,b^*c^*\cos\alpha^* + 2lhc^*a^*\cos\beta^*+2hk\,a^*b^*\cos\gamma^*.$$

Thus for each reflection ($hkl$) there is a linear equation connecting the observable quantity Q with the six functions of the lattice parameters by the known values of $h$, $k$, and $l$. Although only six values of Q are needed for a determination of the six lattice parameters, it is desirable to obtain as many values of Q as possible in order to increase the accuracy of determination.

It was soon found that trial-and-error adjustment of the lattice parameters was tedious and uncertain, and a systematic method was adopted that yields least-squares estimates of the variable quantities $a^{*2}$, $b^*c^*\cos\alpha^*$, &c. The method is based on the standard procedure for the solution of linear equations described by Fisher (1950). Since the method may be used for powder X-ray data of any soda-rich plagioclase and a variation of it may be used for any solid-solution series, a brief account will be given here.

The procedure for calculating the lattice functions $a^{*2}$, $b^{*2}$, $c^{*2}$, $2b^*c^*\cos\alpha^*$, $2c^*a^*\cos\beta^*$ and $2a^*b^*\cos\gamma^*$ of unheated specimen 152 is displayed in table V. The values of $h^2$, $k^2$, $l^2$, $kl$, $lh$, and $hk$ for the set of reflections $20\bar{1}$, $1\bar{1}1$, 111, $1\bar{3}0$, 130, $11\bar{2}$, $\bar{1}12$, $13\bar{1}$, 131, $\bar{1}32$, $24\bar{1}$, $\bar{2}41$, 060, 222, 113, and $20\bar{4}$ are listed as the array $D$, $E$, $F$, $G$, $I$, $J$. The numbers $n$, $o$, $p$, $q$, $r$, $s$ are obtained by multiplying corresponding values of Q and $D$, $E$, $F$, $G$, $I$, $J$, and adding. Thus

$$10^5n = 4\times6132+1\times6645+\ldots+1\times30\,971+4\times31\,698;$$
$$10^5s = 0\times6132+\bar{1}\times6645+\ldots+1\times30\,971+0\times31\,698.$$

The normal equations for this set of reflections, represented in matrix form, are:

$$\begin{Vmatrix} 90 & 194 & 117 & 25 & -39 & 14 \\ 194 & 2234 & 121 & 73 & -47 & -10 \\ 117 & 121 & 408 & 67 & -111 & 13 \\ 25 & 73 & 67 & 121 & 13 & -47 \\ -39 & -47 & -111 & 13 & 117 & 25 \\ 14 & -10 & 13 & -47 & 25 & 194 \end{Vmatrix} \cdot \begin{Vmatrix} u \\ v \\ w \\ x \\ y \\ z \end{Vmatrix} = \begin{Vmatrix} n \\ o \\ p \\ q \\ r \\ s \end{Vmatrix}$$

where $u$, $v$, $w$, $x$, $y$, $z$ are the least-squares estimates of the functions $a^{*2}$, $b^{*2}$, $c^{*2}$,

$2b^*c^*\cos\alpha^*$, $2c^*a^*\cos\beta^*$, $2a^*b^*\cos\gamma^*$. This equation may be transformed into the equation

$$\begin{Vmatrix} u \\ v \\ w \\ x \\ y \\ z \end{Vmatrix} = \begin{Vmatrix} \text{Matrix} \\ A \end{Vmatrix} \cdot \begin{Vmatrix} n \\ o \\ p \\ q \\ r \\ s \end{Vmatrix}$$

where the covariance matrix $A$ is the inverse of the left-hand matrix in the set of normal equations. The numerical values of the covariance matrix $A$ are listed in table VI. In table V the above set of equations is written out in full and the least-squares estimates $u, v, w, x, y, z$ have been calculated from the values of $n, o, p, q, r, s$ derived previously ($R$ and $C$ in table V refer to the row and column of matrix $A'$).

The standard deviation, $\sigma$, of the individual measurements is estimated by $\hat{\sigma}$ where

$$(\hat{\sigma})^2 = \Sigma\,(Q_{obs}-Q_{calc})^2/N-6$$
$$= \frac{\Sigma\,Q^2_{obs}-nu-ov-pw-qx-ry-sz}{N-6}$$

where $N$ is the number of observations, $Q_{calc}$ is the value of $1/d^2$ calculated from the

TABLE V. Calculation form for obtaining reciprocal lattice functions from the observed Q values.

| *hkl.* | *D.* | *E.* | *F.* | *G.* | *I.* | *J.* | $10^5\times Q_{obs.}$ | | $10^5\times Q_{calc.}$ |
|---|---|---|---|---|---|---|---|---|---|
| $20\bar{1}$ | 4 | 0 | 1 | 0 | $\bar{2}$ | 0 | 6132 | $10^5n =$ 5·05706 | 6133 |
| $1\bar{1}1$ | 1 | 1 | 1 | $\bar{1}$ | 1 | $\bar{1}$ | 6645 | $10^5o =$ 19·43690 | 6642 |
| 111 | 1 | 1 | 1 | 1 | 1 | 1 | 7069 | $10^5p =$ 10·99405 | 7074 |
| $1\bar{3}0$ | 1 | 9 | 0 | 0 | 0 | $\bar{3}$ | 7202 | $10^5q =$ 2·99321 | 7203 |
| 130 | 1 | 9 | 0 | 0 | 0 | 3 | 7491 | $10^5r = -1$·48679 | 7495 |
| $11\bar{2}$ | 1 | 1 | 4 | $\bar{2}$ | $\bar{2}$ | 1 | 8237 | $10^5s =$ 1·01662 | 8245 |
| $\bar{1}12$ | 1 | 1 | 4 | 2 | $\bar{2}$ | $\bar{1}$ | 8813 | — | 8817 |
| $1\bar{3}1$ | 1 | 9 | 1 | $\bar{3}$ | 1 | $\bar{3}$ | 11075 | — | 11079 |
| 131 | 1 | 9 | 1 | 3 | 1 | 3 | 12371 | — | 12375 |
| $\bar{1}32$ | 1 | 9 | 4 | 6 | $\bar{2}$ | $\bar{3}$ | 14256 | — | 14258 |
| $24\bar{1}$ | 4 | 16 | 1 | $\bar{4}$ | $\bar{2}$ | 8 | 15606 | — | 15595 |
| $\bar{2}41$ | 4 | 16 | 1 | 4 | $\bar{2}$ | $\bar{8}$ | 16152 | — | 16151 |
| 060 | 0 | 36 | 0 | 0 | 0 | 0 | 21918 | — | 21914 |
| 222 | 4 | 4 | 4 | 4 | 4 | 4 | 28306 | — | 28298 |
| 113 | 1 | 1 | 9 | 3 | 3 | 1 | 30971 | — | 30975 |
| $20\bar{4}$ | 4 | 0 | 16 | 0 | $\bar{8}$ | 0 | 31698 | — | 31693 |

$$u = a^{*2} = nR1C1+oR1C2+pR1C3+qR1C4+rR1C5+sR1C6 = 0{\cdot}18721608$$
$$v = b^{*2} = nR2C1+oR2C2+pR2C3+qR2C4+rR2C5+sR2C6 = 0{\cdot}06087481$$
$$w = c^{*2} = nR3C1+oR3C2+pR3C3+qR3C4+rR3C5+sR3C6 = 0{\cdot}24678439$$
$$x = 2b^*c^*\cos\alpha^* = nR4C1+oR4C2+pR4C3+qR4C4+rR4C5+sR4C6 = 0{\cdot}01670947$$
$$y = 2a^*c^*\cos\beta^* = nR5C1+oR5C2+pR5C3+qR5C4+rR5C5+sR5C6 = 0{\cdot}19100256$$
$$z = 2a^*b^*\cos\gamma^* = nR6C1+oR6C2+pR6C3+qR6C4+rR6C5+sR6C6 = 0{\cdot}00492788$$

$$\Sigma\,Q^2_{obs} - (nu+ov+pw+qx+ry+sz) = 4{\cdot}271\times10^{-7}$$
$$\hat{\sigma}^2 = 4{\cdot}271\times10^{-7}/(16-6) = 4{\cdot}271\times10^{-8}$$

$$\sigma(a^{*2}) = \sqrt{(4{\cdot}271\times10^{-8}\times R1C1)} = 3{\cdot}2\times10^{-5}$$
$$\sigma(b^{*2}) = \sqrt{(4{\cdot}271\times10^{-8}\times R2C2)} = 1{\cdot}6\times10^{-6}$$
$$\sigma(c^{*2}) = \sqrt{(4{\cdot}271\times10^{-8}\times R3C3)} = 4{\cdot}9\times10^{-6}$$
$$\sigma(2b^*c^*\cos\alpha^*) = \sqrt{(4{\cdot}271\times10^{-8}\times R4C4)} = 7{\cdot}6\times10^{-6}$$
$$\sigma(2a^*c^*\cos\beta^*) = \sqrt{(4{\cdot}271\times10^{-8}\times R5C5)} = 8{\cdot}1\times10^{-6}$$
$$\sigma(2a^*b^*\cos\gamma^*) = \sqrt{(4.271\times10^{-8}\times R6C6)} = 5{\cdot}5\times10^{-6}$$

predicted lattice parameters. The standard deviations of the least-squares estimates of $u, v, w, x, y, z$ are given by the product of $\hat{\sigma}$ and the square root of the element on the principal diagonal of the covariance matrix $A$ corresponding to the coefficient. This procedure is shown in table V. The reciprocal and direct lattice parameters may be obtained from $u, v, w, x, y, z$ by the calculation form given by Donnay and Donnay (1952).

TABLE VI. Values of the elements of the covariance matrices $A'$ and $A''$.

| Row. | Column. | Matrix $A'$ number. | Matrix $A''$ number. |
|---|---|---|---|
| 1 | 1 | +0·02347618450 | +0·03238200385 |
| 1 | 2 | −0·00163406513 | −0·00066591061 |
| 2 | 1 | | |
| 1 | 3 | −0·00482351590 | −0·00650073022 |
| 3 | 1 | | |
| 1 | 4 | −0·00253461419 | −0·00141082551 |
| 4 | 1 | | |
| 1 | 5 | +0·00341049343 | +0·00407451374 |
| 5 | 1 | | |
| 1 | 6 | −0·00250871511 | −0·01405724085 |
| 6 | 1 | | |
| 2 | 2 | +0·00057733243 | +0·00055631682 |
| 2 | 3 | +0·00031275979 | +0·00005422679 |
| 3 | 2 | | |
| 2 | 4 | −0·00014515327 | −0·00032088990 |
| 4 | 2 | | |
| 2 | 5 | −0·00002003478 | −0·00017839258 |
| 5 | 2 | | |
| 2 | 6 | +0·00009413930 | +0·00017044361 |
| 6 | 2 | | |
| 3 | 3 | +0·00551545320 | +0·00559225729 |
| 3 | 4 | −0·00324697742 | −0·00326925275 |
| 4 | 3 | | |
| 3 | 5 | +0·00440162048 | +0·00422479977 |
| 5 | 3 | | |
| 3 | 6 | −0·00135923980 | +0·00125130378 |
| 6 | 3 | | |
| 4 | 4 | +0·01305835264 | +0·01522927428 |
| 4 | 5 | −0·00636993768 | −0·00514882007 |
| 5 | 4 | | |
| 4 | 6 | +0·00437749891 | −0·00035348307 |
| 6 | 4 | | |
| 5 | 5 | +0·01542991344 | +0·01649704278 |
| 5 | 6 | −0·00407372798 | −0·00679057469 |
| 6 | 5 | | |
| 6 | 6 | +0·00701710912 | +0·02219432485 |

The most laborious part of the procedure is the calculation of the covariance matrix $A$ from the normal equations. Considerable labour can be saved if the same set of reflections $(hkl)$ are used for more than one powder pattern, since the same covariance matrix $A$ can be used. Even though many reflections are not resolved over the whole composition range, it was possible to find two sets of reflections which between them covered the whole composition range and which contained sufficient

reflections for the attainment of a suitable precision. The first set has already been listed above and in table V, and its covariance matrix, $A'$, is listed in table VI The second set is $20\bar{1}$, $1\bar{1}1$, 130, $11\bar{2}$, $\bar{1}12$, 040, 002, 220, $1\bar{3}1$, 131, $\bar{1}32$, 060, 222, 113, $20\bar{4}$. The covariance matrix $A''$ for this set of reflections is also listed in table VI.

I am indebted to Mr. J. M. Cameron for his assistance in devising this method and to the Applied Mathematics Division of the National Bureau of Standards for the calculation of the two inverse matrices.

In addition to the error caused by the random experimental error there are two other possible sources. The first arises from the calibration obtained from the quartz internal standard. The uncertainty in the measurements of the quartz reflections is about 0·01° in $2\theta$ and results in a corresponding uncertainty in the measurements of the plagioclase reflections. This possible error has little effect on the values for the angles $\alpha^*$, $\beta^*$, and $\gamma^*$, for the coefficients connecting these functions with the values of $Q_{obs}$ are both positive and negative and tend to cancel the errors. For the reciprocal lengths $a^*$, $b^*$, and $c^*$, however, the coefficients are all positive, and an error in calibration gives rise to an error in the reciprocal lengths. The possible error of 0·01° in $2\theta$ corresponds to a possible error of about 1/4000 in $a^*$, $b^*$, and $c^*$. The other source of error arises from displacement of the centre of a peak by interference from adjacent reflections. This effect is difficult to evaluate but is largely included in the estimate of the random experimental error, for any interference from other reflections will tend to increase the differences between the observed and calculated values of Q.

The random errors for unheated specimen 152 correspond to standard deviations of approximately 1/1000 in $a^*$, 1/8000 in $b^*$, 1/10 000 in $c^*$, and 0·01–0·02° in $\alpha^*$, $\beta^*$, and $\gamma^*$. Similar values were found for the other natural plagioclases.[1] The accuracy of the parameters for the synthetic plagioclases is somewhat poorer.

Table III contains the $2\theta$ values of the reflections used in the calculations, and table IV the lattice parameters obtained from the calculations and from the literature.

### *The significance of the lattice parameters.*

The relations between the lattice parameters and the chemical composition are displayed graphically in figs. 1 and 2. The only serious

[1] For one specimen, unheated BM 1940,27, the 130 and $1\bar{3}0$ reflections were unresolved. In order to use the set of reflections A, estimated values of Q were inserted in place of the two unmeasurable values of Q. From the resulting functions of the lattice parameters revised values of Q were calculated and new estimates of the lattice parameters were obtained by insertion of the new values of Q into the calculation procedure.

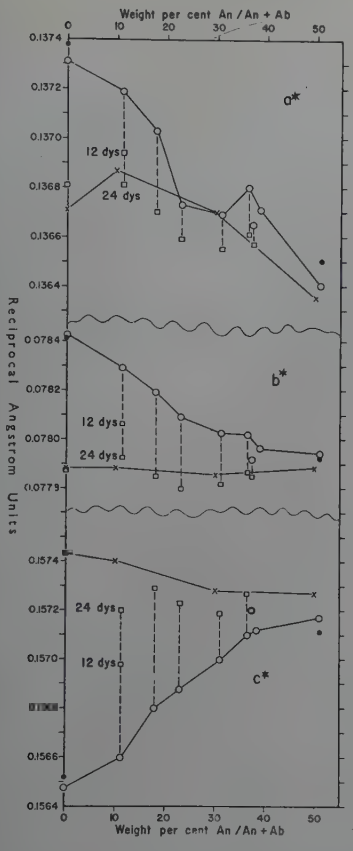


FIG. 1.

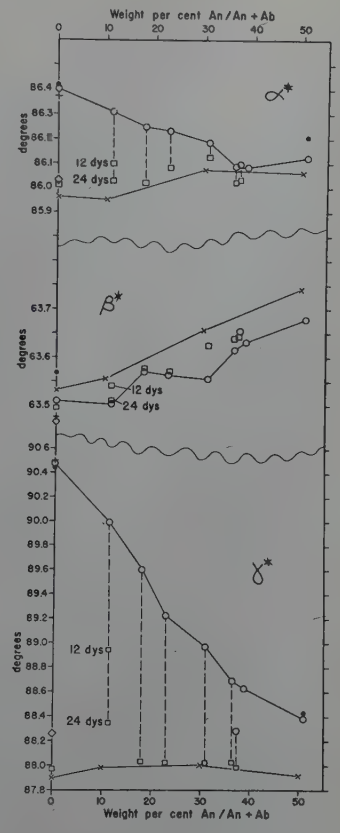


FIG. 2.

FIG. 1. The values of the reciprocal lattice parameters $a^*$, $b^*$, and $c^*$ plotted against chemical composition. The ordinate is expressed in reciprocal Ångströms, the abscissa in weight % of the anorthite component. Notice the changes of scale for the ordinates. ○ natural, present work; □ heated natural, present work; × synthetic, present work; ● natural, Cole *et al.*; ◇ heated natural, Laves. The captions 12 dys and 24 dys denote specimens heated for 12 and 24 days at 1060° C. The data are given in table IV.

FIG. 2. The values of the reciprocal lattice parameters $\alpha^*$, $\beta^*$, and $\gamma^*$ plotted against anorthite content. Notice the changes of scale for the ordinates. ○ natural, present work; □ heated natural, present work; × synthetic, present work; ● natural, Cole *et al.*; ◇ heated natural, Laves. The data are given in table IV.

discrepancy between the values obtained by other workers and those in the present work is the value of $\gamma^*$ for heated Amelia albite listed by Laves (1952); this specimen was probably only partly converted into

the high-temperature state. Otherwise the measurements obtained in this work agree within the possible errors with those obtained by other workers from single-crystal patterns.

Eight out of the nine natural plagioclases occur in low-temperature environments; that is, environments in which the plagioclase should have had ample opportunity to attain the form stable at low temperatures. The remaining one is from a dacite. In conformity with this division the lattice parameters of the eight low-temperature plagioclases lie, within experimental error, on continuous curves, while the parameters of the volcanic specimen are considerably displaced.

During strong heating followed by quenching, the lattice parameters of the natural plagioclases slowly changed. For six of the specimens the final state (or a good approximation to it) was established, and the resulting lattice parameters lie fairly closely on another set of continuous curves. One of the specimens, BM 1940,27, did not reach equilibrium but would probably have done so if further heating had been applied. The lattice parameters of the unheated volcanic specimen lie approximately midway between the two sets of curves, thus indicating a transitional thermal state for this specimen. Gay (1955) also finds evidence for a transitional state from the subsidiary reflections on single-crystal photographs. The existence of this transitional state suggests that the attainment of equilibrium is very slow; and in conformity with this, all synthetic soda-rich plagioclases so far produced are in the high-temperature state.[1]

The lattice parameters of the synthetic plagioclases used in this study lie on a set of curves that are continuous within experimental error. One of the specimens was produced hydrothermally ($An_0$), the others ($An_{10}$, $An_{30}$, and $An_{50}$) were grown in the dry state.[2] Although the curves lie close to the data for the heated natural material there are deviations that are greater than the experimental error. It is thought that these deviations are caused by the solid solution of potash felspar in the natural plagioclases. The chemical analyses of those natural specimens that were converted into the high-temperature state reveal the following amounts of potash-felspar in solid solution: Amelia, 1·8 %; No. 81822,

[1] MacKenzie and Smith, however (Nov. 1955 meeting of the Geological Society of America), have recently produced synthetic albite with an X-ray powder pattern intermediate between high- and low-albite.

[2] A specimen of composition $An_{40}$ gave a powder pattern that contained the lines of a plagioclase together with a line in the position of the strongest line of hexagonal anorthite (Davis and Tuttle, 1952). In view of the uncertainty in the composition of the plagioclase this specimen was disregarded.

1·3 %; No. 103086, 3·5 %; No. 97490, 3·6 %; No. 152(6), 1·5 %; and No. 64(7), 3·2 %. The lattice parameters of the three specimens with less than 2 % $KAlSi_3O_8$ lie closer to the values for the synthetic plagioclases than do the parameters for the other three specimens. Moreover, the deviations lie, on the average, in the same direction as the changes produced in the lattice parameters of the high-temperature alkali-felspars by substitution of potash (Donnay and Donnay, 1952). The magnitudes of the deviations are only one-half to one-third of the changes produced in high-albite by an equivalent amount of potash, which suggests that, if the deviations are indeed caused by potash, the effect of potash content decreases with increasing lime content.

It is probable, therefore, that structurally there is only one series[1] of high-temperature soda-rich plagioclases. By slow cooling or growth at low temperatures a series of low-temperature soda-rich plagioclases is produced. Specimens may exist in all stages between these two extremes.

There is no measurable discontinuity in the lattice parameters of the high-temperature material, thus conforming with the evidence obtained by Bowen (1913) from melting phenomena, by Gay (1955) from single-crystal phenomena, and by Goodyear and Duffin (1954) from powder X-ray data, that complete solid-solution occurs just below the solidus in soda-rich plagioclases.

The lattice parameters of the high-temperature soda-rich plagioclases are almost independent of composition; the substitution of 50 % An results in the following changes: $a^*$ 1/400, $b^*$ zero, $c^*$ 1/100, $\alpha^*$ 0·1°, $\beta^*$ 0·2°, $\gamma^*$ zero. These changes are so small that there is no reliable routine method for determining the composition of high-temperature soda-rich plagioclases from the angular relations displayed in X-ray photographs. The largest change, that in $\beta^*$, is only ten times the experimental error of 0·02°, and, moreover, the substitution of small amounts of potash felspar in high-albite (Donnay and Donnay, 1952) produces changes comparable with those produced by much larger amounts of anorthite.

In contrast to the high-temperature plagioclases the natural low-temperature plagioclases show large changes in the lattice parameters. From $An_0$ to $An_{50}$ the changes are as follows: $a^*$ −1/150, $b^*$ −1/150, $c^*$ +1/200, $\alpha^*$ −0·3°, $\beta^*$ +0·2°, $\gamma^*$ −1·8°. The largest change is in $\gamma^*$, and this is the basis of all the methods proposed for the determination of composition of soda-rich plagioclases from powder records. It is

[1] Neglecting the very small differences between X-ray properties of synthetic albite produced hydrothermally and in the dry way (MacKenzie, 1952).

interesting to note that all the high-temperature plagioclases, together with those low-temperature plagioclases which are more calcic than $An_{10}$, have $\gamma^*$ acute, whereas the low-temperature plagioclases from $An_0$ to $An_{10}$ have an obtuse value for $\gamma^*$.

There is no evidence for a discontinuity or sharp change in gradient in the variation of lattice parameters with composition for the natural low-temperature specimens. Examination of the graphs for the more sensitive parameters $\gamma^*$, $b^*$, and $c^*$ shows that the gradient of the curves becomes gradually less steep as the anorthite content increases. The curves tend to become asymptotic to the very flat curves for the high-temperature specimens. (The zigzag in $a^*$ could be caused either by the comparatively large potash content of specimens 103086 and 97490 or by the experimental error of 1/1000.) Goodyear and Duffin (1954) report that

> the A—B, C—D and C—E curves for the natural materials each show prominent discontinuities reasonably close to the structural discontinuities at $An_{30}$ $Ab_{70}$ and $An_{70}$ $Ab_{30}$ proposed by Cole *et al.* (1951). These are significant as each of these reflections (A, B, C, D, and E) probably has the same, or similar, indices over the whole composition range.

The present observations are not in harmony with the findings of Goodyear and Duffin.

*The determination of soda-rich plagioclases by X-ray powder photography.*

One of the important developments of the past decade has been the increasing use of indirect physical methods in the determination of chemical composition, thus by-passing the more tedious methods of analytical chemistry. In some mineral groups (e.g. alkali felspars and nephelines) it has been shown that the ratio of the two dominant oxides (such as $Na_2O$ and $K_2O$) can be determined by X-ray powder methods in a few minutes as a matter of routine. Similar methods for determining the composition and thermal state of plagioclases would be extremely useful.

Unfortunately the present work shows that there is no routine X-ray powder method available for the accurate determination of both the composition and the thermal state of soda-rich plagioclases. Five of the lattice parameters for the intermediate states given by the heated specimen BM 1940,27, composition $An_{11}$, are identical within experimental error with the parameters given by a low-temperature specimen of higher anorthite content. The specimen heated for 12 days has $a^*$, $b^*$, $c^*$, $\alpha^*$, and $\gamma^*$ indistinguishable from those given by a low-temperature plagioclase of composition $An_{30}$. The same five parameters for

BM 1940,27, heated 24 days, and for the specimen from a dacite, composition $An_{37}$, are identical within experimental error and correspond to a low-temperature plagioclase of composition greater than $An_{50}$ (extrapolated from the curves). The remaining parameter, $\beta^*$, is different: the values of $\beta^*$ for the plagioclase from the dacite and for BM 1940,27, heated 24 days, differ by 0·14°. Thus only $\beta^*$ is sufficiently different to provide a distinction, and even here the difference is so small that the composition could not be determined with an accuracy higher than 5–10 % An: the determination of the thermal state would also be crude. In routine work the best that can be obtained from powder patterns alone is an upper limit to the anorthite content. Thus if $\gamma^*$ was found to be 90·0°, then the anorthite content must be less than 11 %.

However, by combining powder X-ray data with petrological, optical, and chemical data much valuable information can readily be obtained. Of the two variables, chemical composition and thermal state, one can be determined by X-ray powder methods if the other is known. If the $CaO/Na_2O$ ratio is known, the simplest way of determining the thermal state is by powder X-ray data. The other two methods for determining the thermal state—single-crystal X-ray or optical determinations—are much more tedious and not so suitable for routine application. The $CaO/Na_2O$ ratio can either be determined by the standard chemical or physico-chemical methods or approximated by the measurement of refractive indices. If the plagioclase can be adjudged to be in the low-temperature state the $CaO/Na_2O$ ratio can readily be determined from X-ray powder patterns. Specimens that are taken from large plutonic masses or that have been regionally metamorphosed should be in the low-temperature state. The thermal state of specimens taken from volcanic, hypabyssal, and small plutonic masses must be regarded as uncertain. Specimens that show schiller in the hand-specimen are probably in the low-temperature state. Unmixed albite-oligoclases may reveal their low-temperature state in well-resolved powder records so long as the proportions of the two phases are roughly equal. The presence of peristeritic unmixing of albite-oligoclases is readily seen in suitable single-crystal X-ray photographs, and so are the subsidiary layer-lines of intermediate specimens, but single-crystal methods are not so suitable for routine work, for plagioclases exhibit complex pseudo-symmetry and are anorthic.

The choice of X-ray reflections for the two determinative methods is complicated by the overlapping of otherwise suitable reflections, which is especially serious for $(hk0)$ and $(h\bar{k}0)$ reflections, which cross over as $\gamma^*$

passes through 90°, and by the presence of two separate phases in low-temperature albite-oligoclases. The latter imposes a contradictory condition on the choice of reflections. In order to obtain the highest accuracy one normally chooses the reflections that move the most; however, if the reflections for the two phases in the peristerite move a long way they may become partly resolved and produce a false measurement. For if the peaks are partly resolved and one phase is more abundant than the other it is likely that only the strong peak would be measured. For the highest accuracy in the peristerite region it is necessary to choose reflections which move about half the width of the peaks and to measure the centre of gravity of the peaks. Two sets of adjacent peaks satisfy this condition: (111) and (1$\bar{1}$1), which occur at $2\theta_{Cu} = 23{\cdot}6 \pm 0{\cdot}1°$ and $23{\cdot}0 \pm 0{\cdot}1°$, respectively; and ($\bar{1}$32) and (131), which occur at $2\theta_{Cu} = 33{\cdot}85 \pm 0{\cdot}1$ and $31{\cdot}4 \pm 0{\cdot}15°$, respectively. In the remaining composition range, the two most suitable reflections appear to be the ones used by Tuttle and Bowen—the (131) and (1$\bar{3}$1), which occur at $2\theta_{Cu} = 31{\cdot}4 \pm 0{\cdot}15°$ and $29{\cdot}9 \pm 0{\cdot}25°$. This pair of reflections is not suitable in the peristerite region, for the (1$\bar{3}$1) reflection is often unresolved from adjacent reflections and, moreover, moves too far. In the remainder of the plagioclase series both reflections are fully resolved. The (2$\bar{2}$0), ($\bar{1}$32), (24$\bar{1}$), and ($\bar{2}$41) reflections have been used, first by Claisse and then by Goodyear and Duffin, but they are not suitable in the peristerite region, for they move too fast with composition and the (2$\bar{2}$0) and (220) reflections cross over. Nor are the latter three reflections suitable in the region above $An_{70}$, for the (24$\bar{1}$) and ($\bar{2}$41) reflections cross over. In the remaining region, $An_{20}$–$An_{70}$, they are very suitable for low-temperature specimens, but are not so suitable for high-temperature specimens, again because of the poor resolution between the (24$\bar{1}$) and ($\bar{2}$41) reflections.

The following procedures are recommended for the two determinations:

*Determination of the thermal state.*

If the anorthite content lies between $An_{20}$ and $An_{40}$, measure the angular separation $2\theta\,(131) - 2\theta\,(1\bar{3}1)$ and determine the thermal state from fig. 3, which is a graph of $2\theta\,(131) - 2\theta\,(1\bar{3}1)$ against composition for all the specimens used for the determination of lattice parameters together with some extra ones. If the anorthite content lies between $An_0$ and $An_{20}$, measure the separation $2\theta\,(\bar{1}32) - 2\theta\,(131)$ and compare with fig. 4, which shows the variation of $2\theta\,(\bar{1}32) - 2\theta\,(131)$ with chemical composition and thermal state. If the thermal state is found to be low-

temperature, measure $2\theta\,(111)-2\theta\,(1\bar{1}1)$ as a check and compare with fig. 5, which shows the variation of $2\theta\,(111)-2\theta\,(1\bar{1}1)$ with chemical composition for low-temperature albites and oligoclases. If the thermal state is found to be high-temperature or intermediate, measure $2\theta\,(131)-2\theta\,(1\bar{3}1)$ as a check and compare with fig. 3.

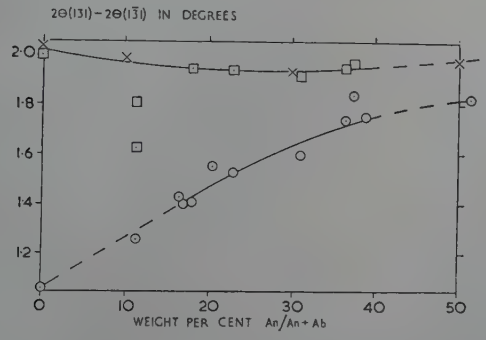


FIG 3. The values of $2\theta\ (131) - 2\theta\,(1\bar{3}1)$ plotted against chemical composition. ○ natural; □ heated natural; × synthetic. The data are listed in table VII.

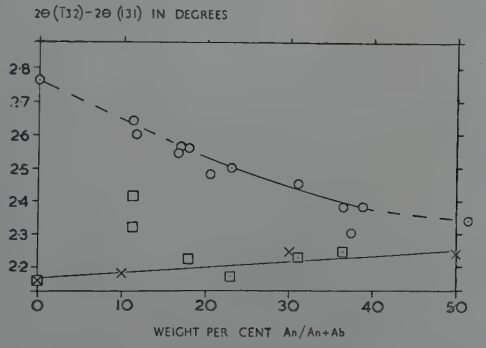


FIG. 4. The values of $2\theta\ (\bar{1}32) - 2\theta\ (131)$ plotted against chemical composition. ○ natural; □ heated natural; × synthetic. The data are listed in table VII.

*Determination of the composition of low-temperature specimens.*

If the thermal state is adjudged to be low-temperature, measure $2\theta\,(131)-2\theta\,(1\bar{3}1)$ and compare with fig. 3. If the measurement indicates a composition lying between $An_0$ and $An_{20}$, measure either or both of

$2\theta\,(\bar{1}32)-2\theta\,(131)$ and $2\theta\,(111)-2\theta\,(1\bar{1}1)$ and compare with figs. 4 and 5. The resultant composition should be more reliable than the composition deduced from $2\theta\,(131)-2\theta\,(1\bar{3}1)$.

The data for the construction of figs. 3, 4, and 5 are given in table VII.

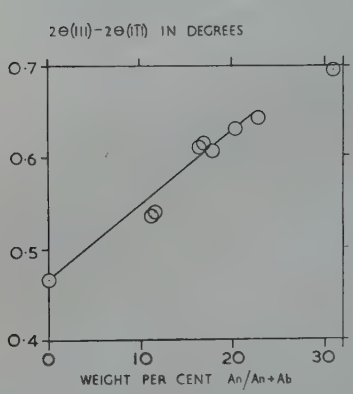


FIG. 5. The values of $2\theta$ (111) $- 2\theta$ ($1\bar{1}1$) plotted against chemical composition for natural low-temperature specimens. The data are listed in table VII.

The accuracy of determination of composition or thermal state is rather difficult to estimate. Unfortunately the plagioclase powder pattern is so complex that the peaks tend to be rather weak, the only prominent one being the composite peak at $2\theta_{Cu} = 28°$ composed largely of the (002) and (040) reflections. It is advisable, therefore, to use only samples in which the plagioclase is the major component. The (131) and ($1\bar{3}1$) reflections are among the strongest ones in the region around $2\theta = 30°$. The ($\bar{1}32$) is rather weaker, and it may often be found preferable to use the pair (111) and ($1\bar{1}1$) in preference to (131) and ($\bar{1}32$). Assuming optimum conditions, it is likely that the precision of measurement can reach 0·005 to 0·02° in $2\theta$ for the expenditure of 10 to 20 minutes running-time of a diffractometer (Smith and Sahama, 1954). In photographic powder cameras the precision is likely to be lower. In addition to this error, the presence of potash or other oxides in the plagioclase may lead to uncertainty in the interpretation of the measurement. It seems likely that in the region $An_0$–$An_{30}$ the composition of low-temperature specimens can be determined with an accuracy of 2 % An and that a clear differentiation of the thermal states can be obtained.

In conclusion, there are a few minor points concerning the work of Goodyear and Duffin. The *F* and *G* reflections of Goodyear and Duffin have the following indices: *G*, (204); *F*, probably mainly ($04\bar{3}$), but includes other reflections as well. Diffractometer records of reflection *F* often show a complex structure and it is doubtful whether it is suitable for measurement. In fig. 2 and table IV of Goodyear and Duffin's paper the reflection (131) is missing, although it is one of the strongest reflections near $2\theta = 31°$. Probably it was masked by a rock-salt reflection.

TABLE VII. Data for figs. 3, 4, and 5. All values are for the estimated centre of gravity of the $\alpha_1+\alpha_2$ doublet. An/(An+Ab) is given in weight %. The values of $2\theta$ are in degrees, and the accuracy of the measurements lies between 0·005 and 0·02°.

| Specimen | An/(An+Ab) | $2\theta_{(111)}-2\theta_{(1\bar{1}1)}$ | $2\theta_{(131)}-2\theta_{(1\bar{3}1)}$ | $2\theta_{(\bar{1}32)}-2\theta_{(131)}$ |
|---|---|---|---|---|
| Amelia unheated ... ... ... | 0·0 | 0·467 | 1·062 | 2·766 |
| Amelia heated ... ... ... | 0·0 | — | 1·990 | 2·16 |
| BM 1940,27 unheated ... ... | 11·2 | 0·537 | 1·255 | 2·643 |
| BM 1940,27; 12 days 1060° C. ... | 11·2 | — | 1·625 | 2·415 |
| BM 1940,27; 24 days 1060° C. ... | 11·2 | — | 1·805 | 2·320 |
| Emmons 10(2) unheated ... | 11·6 | 0·540 | not measurable | 2·630 |
| Emmons 73(3) unheated ... ... | 16·6 | 0·610 | 1·425 | 2·575 |
| Emmons 156(4) unheated ... | 16·9 | 0·615 | 1·390 | 2·595 |
| 81822 unheated ... ... ... | 17·9 | 0·605 | 1·405 | 2·560 |
| 81822 heated ... ... ... | 17·9 | — | 1·940 | 2·225 |
| Emmons 94(5) unheated ... ... | 20·4 | 0·630 | 1·550 | 2·510 |
| 103086 unheated ... ... ... | 22·9 | 0·642 | 1·525 | 2·500 |
| 103086 heated ... ... ... | 22·9 | — | 1·930 | 2·170 |
| 97490 unheated ... ... ... | 31·0 | 0·694 | 1·595 | 2·462 |
| 97490 heated ... ... ... | 31·0 | — | 1·912 | 2·228 |
| Emmons 152(6) unheated ... | 36·4 | — | 1·735 | 2·380 |
| Emmons 152(6) heated ... ... | 36·4 | — | 1·948 | 2·245 |
| Emmons 64(7) unheated ... ... | 37·3 | — | 1·840 | 2·300 |
| Emmons 64(7) heated ... ... | 37·3 | — | 1·963 | 2·225 |
| Emmons 144(8) unheated ... | 38·8 | — | 1·750 | 2·380 |
| Emmons 24(9) unheated ... ... | 50·9 | — | 1·813 | 2·340 |
| Synthetic ... ... ... ... | 0 | — | 2·030 | 2·160 |
| Synthetic ... ... ... ... | 10 | — | 1·980 | 2·180 |
| Synthetic ... ... ... ... | 30 | — | 1·930 | 2·245 |
| Synthetic ... ... ... ... | 50 | — | 1·975 | 2·240 |

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# *On the correlation of physical properties with chemical composition in multivariate systems*

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[Read 27 January 1955.]

*Summary.*—A systematic and time-saving procedure for the correlation of optical or other physical properties with chemical composition is outlined, and is applicable even where the composition is complex and involves several variables. The procedure is applied to anthophyllite, for which the following partial regression equations are derived:

$$\gamma = 1{\cdot}7249 - 0{\cdot}0130\mathrm{Si} + 0{\cdot}0140(\mathrm{Ti} + \mathrm{Fe'''} + \mathrm{Fe''} + \mathrm{Mn}) \pm 0{\cdot}0012,$$
$$\beta = 1{\cdot}7275 - 0{\cdot}0142\mathrm{Si} + 0{\cdot}024(\mathrm{Ti} + \mathrm{Fe'''}) + 0{\cdot}0110(\mathrm{Fe''} + \mathrm{Mn}) \pm 0{\cdot}0015,$$
$$\alpha = 1{\cdot}6951 - 0{\cdot}0117\mathrm{Si} + 0{\cdot}040(\mathrm{Ti} + \mathrm{Fe'''}) + 0{\cdot}0133(\mathrm{Fe''} + \mathrm{Mn}) \pm 0{\cdot}0025,$$
$$b\ (\text{Å}.) = 16{\cdot}44 + 0{\cdot}28\mathrm{Si} - 0{\cdot}13\ \mathrm{Mg} + 0{\cdot}40(\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}04.$$

The $a$ and $c$ cell-dimensions appear to be constant, within the experimental error of the available data.

BY far the most popular as well as the simplest means of deriving and displaying the correlation of the physical properties of a mineral with its chemical composition is the graphical method, either in the form of a linear graph or a triangular or square contoured correlation diagram; but these methods are necessarily limited to minerals whose variations in composition can be expressed in terms of one or two parameters,[1] and only the simple linear graph can indicate efficiently the probable accuracy of the correlation.

The method of least squares is applicable to both linear and non-linear correlations with any number of independent parameters, and is widely used in many branches of the physical and biological sciences, but has rarely been applied in mineralogy. Probably one reason for this neglect is the lack of any readily available description of the method as applied to multivariate systems, for such well-known textbooks as J. W. Mellor's 'Higher Mathematics for Students of Chemistry and Physics' (London, 1931) and R. A. Fisher's 'Statistical Methods for Research

[1] The triangular diagram involves three variables, the square one four, but in each case only two are independent.

Workers' (11th edn., Edinburgh, 1950) only devote a few short paragraphs to it, and many only deal with its application to simple correlations with one independent parameter ($y = ax+b$), for which the familiar graphical method is usually adequate. Another reason for this neglect is the assumption that the procedure, as applied to a multivariate system, is necessarily very time-consuming; the evaluation of a determinant of high order is at best a slow process and needs careful checks, and at first glance a set of regression equations in $n$ independent variables would appear to involve the evaluation of $n+1$ determinants of $n$th order for each dependent variable, plus ancillary calculations: the procedure outlined below calls for little more labour than is involved in the calculation of 2 to 4 determinants of the $n$th order, whatever the number of variables.

In many minerals the principal physical properties, including unit-cell dimensions, density, refractive indices, and birefringences, appear to be reasonably well reproduced by linear partial regression equations in which the independent parameters define the chemical composition; they may be weight percentages, empirical unit-cell contents, or atomic ratios (the last will usually be most convenient). The possibility of a non-linear regression must always be borne in mind; perhaps the simplest check is, after deriving the best linear correlation, to plot the residuals (that is, the differences between the observed values of the dependent variable and the value calculated from the regression equation) against each of the compositional parameters in turn. The points should lie evenly about a straight line parallel to the composition axis; if they appear to lie evenly about a straight line not parallel to the composition axis, the regression coefficient for that constituent has been incorrectly estimated, while if they suggest a curve, the correlation is probably non-linear in that constituent.[1]

Before proceeding to discuss methods for deriving regression equations, certain inherent limitations to their use should, perhaps, be emphasized. A regression equation can only be utilized for one particular purpose—an equation or set of equations derived to predict the refractive index or indices of a mineral, given the chemical composition, cannot properly be used to predict the composition, given the refractive indices. The reason for this restriction is clearly explained and illustrated by M. J. Moroney.[2] If it is desired to predict the chemical composition, given an

[1] M. H. Hey, Min. Mag., 1954, vol. 30, pp. 281–4.

[2] M. J. Moroney, Facts from Figures, 2nd edn., Harmondsworth, 1953, pp. 293–4.

adequate number of physical data, a suitable set of regression equations must be calculated for that purpose.[1]

*The derivation of a partial regression equation; selection of data*

The first steps in the investigation of any correlation are to decide on the relevant variables and to review all the available data. As a rule, the independent variables will be parameters defining the chemical composition, and the only question will be how many such parameters are really essential to the correlation: every additional variable increases the order of the determinants involved and adds greatly to the labour of calculation; on the other hand, whereas it is a relatively simple matter to discard a superfluous variable, the whole investigation has to be repeated if it should be found later that some neglected variable is really essential to the correlation (e.g. if some supposedly unimportant constituent such as fluorine proves to have an important effect on a physical constant such as the refractive index).

Having decided on the relevant variables and collected all the available data, we have to decide whether all the data should or can be used, and whether all should be assigned equal weight. Generally speaking, it is desirable to make the fullest use of all available data, but it will be obvious that if part of the data is more accurate than the rest, it should be given greater weight.[2] Occasionally it may happen that a part of the data is much more accurate than the rest; then it may be desirable to derive the regression equation from the more accurate data alone, and check the result by comparison of predictions made using this equation with the remaining, less accurate data. Similarly, a few sets of data of doubtful accuracy are best rejected for the derivation of the regression equation.

If several physical quantities, such as refractive indices, density,

[1] This has been done for the mineral here taken as an example, anthophyllite, but owing to the restricted range of variation of the birefringences the results will always be rather inaccurate. The equations derived for the composition, in atoms per 24(O,OH,F), and assuming an accuracy of $\pm 0{\cdot}001$ in the refractive indices and $\pm 0{\cdot}03$ in the density, are:

$$\begin{aligned}
\mathrm{Si} &= 165\,(\gamma-\beta)-102\,(\gamma-\alpha)-30\gamma-3{\cdot}3D+60{\cdot}13\pm 0{\cdot}5,\\
\mathrm{Al} &= -346\,(\gamma-\beta)+229\,(\gamma-\alpha)+29\gamma+10{\cdot}8D-81{\cdot}70\pm 1{\cdot}0,\\
\mathrm{Mg} &= -33\,(\gamma-\beta)+37\,(\gamma-\alpha)-61\gamma+0{\cdot}2\,D+103{\cdot}87\pm 0{\cdot}5,\\
\mathrm{Fe}'' &= 103\,(\gamma-\beta)-10\,(\gamma-\alpha)-50\gamma+18{\cdot}3\,D+24{\cdot}59\pm 0{\cdot}4.
\end{aligned}$$

These equations give a fairly satisfactory representation of the ten superior sets of data by J. C. Rabbitt (see below).

[2] The procedure for giving greater or less weight to a part of the data is discussed below, p. 91.

unit-cell dimensions, &c., are to be correlated with the same group of independent variables, such as parameters defining the composition, it will almost always be advantageous to reject any sets of observations in which only some of the physical quantities were determined (provided there are not too many such sets). The reason for this is that if the independent variables are the same for all the sets of observations utilized, a single covariance matrix can be calculated and applied to derive the regression equations for all the physical quantities; and, as will be seen below, the calculation of the covariance matrix is the most laborious stage in the calculations. But calculated values for any rejected data should always be derived and compared with the observations, as a check.

It is perhaps preferable, in discussing the derivation of a set of partial regression equations, to consider a concrete example, and the correlation of the refractive indices and unit-cell dimensions of anthophyllite with its composition is a useful one, because it is not too simple, but illustrates well many of the possible complications. The available optical data consist of some thirty-eight sets of data obtained on analysed specimens,[1] but in some cases only one refractive index or only the optic axial angle was determined; moreover, ten sets of data, all determined by one worker and therefore more strictly comparable, are of decidedly superior accuracy. The X-ray data consist of ten sets of cell-dimensions, on a group of analysed specimens[2] overlapping the group with optical data of superior accuracy. The variations in the $a$ and $c$ dimensions are within the accuracy of the measurements, but the $b$ dimension shows significant variation.

The first step was to select suitable parameters to define the composition. Anthophyllite may have at least fourteen composition variables: Si, Ti, Al, Fe‴, Fe″, Mn, Mg, Ca, Na, K, F′, OH′, O″, and interstitial $H_2O$ (as in the Glen Urquhart gedrite); but only thirteen of these will be independent, on account of the valency balance.

The composition would be best expressed in empirical unit-cell contents, but the regression equations could then only be used where the necessary density and cell-dimensions were available. If empirical unit-

[1] Analyses 1, 2, 3, 4, 6, 7, 8, 9, 10, 13, 14, 15, 16, 17, 20, 22, 24, 25, 26, 29, 30, 33, 34, 35, 38, 39, 40, 41, 43, 44, 45, 72, 79a, and 85 of J. C. Rabbitt (Amer. Min., 1948, vol. 33, p. 263 [M.A. **10**–416]); R. Pirani, Atti (Rend.) Accad. Naz. Lincei, cl. fis. mat. nat., 1952, ser. 8, vol. 13, sem. 2, p. 83 [M.A. **12**–30], and p. 170 [M.A. **12**–140], and 1953, vol. 15, sem. 2, p. 422 [M.A. **12**–374]; G. H. Francis, Min. Mag., 1955, vol. 30, p. 709.

[2] J. C. Rabbitt's nos. 1, 8, 9, 14, 17, 20, 26, 29, 30, and 43.

cell contents are not used, some assumption must be made, and it is convenient to assume that $\sum$ (O,OH,F) = 96, neglecting the possibility of interstitial water; in fact, none of the ten selected analyses shows any interstitial $H_2O$, so this parameter is not required, though, as will be seen below, interstitial $H_2O$ appears to have a very marked effect on the refractive indices. The number of parameters has thus been reduced to eleven. Owing to the small number of analyses in which it was sought, F′ was necessarily neglected; this is unfortunate in view of the large effect it usually has on the refractive indices. Variations in OH′ were also neglected in view of the uncertainties relating to the water determinations. Further, in view of the small amounts of Ti and Fe‴ present, and their similar optical effects, (Ti+Fe‴) was taken as one variable for the optical data; similarly, (Ca+Na+K) was taken as one variable, and Mn was included with Fe″. The reduced number of independent parameters is six: Si, Al, (Ti+Fe‴), (Fe″+Mn), Mg, and (Ca+Na+K). Finally, it has been assumed that the replacements Ti $\rightleftharpoons$ Fe, Ca $\rightleftharpoons$ (Na, K), and O $\rightleftharpoons$ (OH,F) can be set against one another and balanced out within the probable accuracy of the chemical analyses; with this restriction, the requirement of valency balance reduces the number of independent parameters to five. It is convenient to discard Al as an independent parameter, leaving for the correlation with the optical data: Si, (Ti+Fe‴), (Fe″+Mn), Mg, and (Ca+Na+K), all expressed in atoms per 24(O,OH,F); the unit of 24(O,OH,F) was chosen to facilitate comparison with the clinoamphiboles and the pyroxenes.

For the correlation with the unit-cell dimensions it may reasonably be assumed that in view of their similar ionic radii the small amounts of Mn may be included with Fe″, and the Ti and Fe‴ with Al, while Ca, Na, and K may be taken together. And in view of the uncertainty of some of the water contents, and the similarity in the radii of F′, OH′, and O″, the variations in $H_2O$ and F′ have been disregarded. The number of variables is thus reduced to five, only four of which are independent; these are the same as for the correlation with the refractive indices, excluding Ti+Fe‴.

The next step is to decide whether to use the whole or a selected part of the available optical data (all the X-ray data are useful and of about equal weight). The use of incomplete sets of data would have the disadvantage that a complete recalculation of the covariance matrix (see below, p. 78) would be needed in respect of that optical constant for which additional data was available, and the incomplete data were not numerous, nor did they extend the composition field notably; they were

TABLE I. X-ray and selected optical data for analysed specimens of anthophyllite. Chemical data are given in atoms per 24(O,OH,F). The inferior optical data in square brackets are not included in the means. $M_o$ gives the means of the ten sets of data used for the optical correlations, nos. 1, 8, 9, 14, 17, 22, 26, 29, 30, and 35, while $M_x$ gives the means of the ten sets used for the X-ray correlation, nos. 1, 8, 9, 14, 17, 20, 26, 29, 30 and 43.

| No.* | Si. | Ti+Fe‴. | Fe″+Mn. | Mg. | Ca+Na+K. | $\gamma$. | $\beta$. | $\alpha$. | $b$(Å.) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 6·20 | 0·15 | 2·23 | 3·37 | 0·41 | 1·6781 | 1·6670 | 1·6566 | 17·96 |
| 8 | 6·50 | 0·35 | 1·83 | 3·78 | 0·08 | 1·6718 | 1·6630 | 1·6553 | 17·86 |
| 9 | 6·60 | 0·12 | 2·08 | 3·93 | 0·12 | 1·6695 | 1·6603 | 1·6520 | 17·84 |
| 14 | 6·82 | 0·17 | 1·71 | 4·34 | 0·02 | 1·6619 | 1·6545 | 1·6476 | 17·70 |
| 17 | 7·01 | 0·28 | 2·11 | 3·67 | 0·29 | 1·6671 | 1·6595 | 1·6540 | 17·99 |
| 20 | 7·42 | 0·69 | 2·02 | 2·67 | 0·00 | [1·672] | [1·6667] | [1·656] | 18·14 |
| 22 | 7·77 | 0·19 | 2·48 | 4·09 | 0·04 | 1·6605 | 1·6490 | 1·6454 | — |
| 26 | 7·83 | 0·15 | 1·85 | 4·83 | 0·08 | 1·6517 | 1·6384 | 1·6329 | 18·08 |
| 29 | 7·85 | 0·00 | 1·00 | 5·95 | 0·37 | 1·6350 | 1·6270 | 1·6180 | 17·94 |
| 30 | 7·84 | 0·00 | 1·27 | 5·51 | 0·16 | 1·6410 | 1·6280 | 1·6162 | 18·02 |
| 35 | 7·96 | 0·00 | 1·22 | 5·91 | 0·03 | 1·6404 | 1·6301 | 1·6195 | — |
| 43 | 7·76 | 0·03 | 0·32 | 6·04 | 0·31 | — | [1·62] | — | 17·94 |
| $M_o$ | 7·24 | 0·14 | 1·78 | 4·54 | 0·16 | 1·6577 | 1·6477 | 1·6397 | — |
| $M_x$ | 7·18 | 0·19 | 1·64 | 4·41 | 0·19 | — | — | — | 17·95 |

* The numbers are those assigned by J. C. Rabbitt, Amer. Min., 1948, vol. 33, p. 263 [M.A. **10**–416]; reference should be made to this paper for localities and other information.

therefore not used for the calculation of the partial regression equations. An attempt was made to derive equations using all the remaining data, and assigning a weight of 2 to J. C. Rabbitt's data in view of their superior accuracy; but the equations so deduced gave residuals[1] for the superior data that were unexpectedly high and distinctly biased, suggesting that not enough weight had been given to the superior data.

It would indeed appear that the difference between the accuracy and coherence of J. C. Rabbitt's optical data and that of the rest cannot adequately be met by a weighting factor, and as Rabbitt's data appear to cover the composition field reasonably well, a fresh start was made, using them alone (analyses 1, 8, 9, 14, 17, 22, 26, 29, 30, and 35); their number is uncomfortably small, and it is probable that the equations now deduced will require considerable amendment and extension when more data are available.

*Preliminary preparation of the data; formation of the matrix equations.*

Having ascertained the relevant variables and selected the data, the next step is to reduce the data to a form suitable for computation. First, the mean of each physical quantity and compositional parameter over all the sets of observations is calculated; this is done for our example in

TABLE IIA. Selected optical data for analysed specimens of anthophyllite, expressed as differences from the means ($M_o$) of table I. $S = \mathrm{Si} - \overline{\mathrm{Si}}$, $T = \mathrm{Ti} + \mathrm{Fe}''' - \overline{\mathrm{Ti} + \mathrm{Fe}'''}$, $F = \mathrm{Fe}'' + \mathrm{Mn} - \overline{\mathrm{Fe}'' + \mathrm{Mn}}$, $M = \mathrm{Mg} - \overline{\mathrm{Mg}}$, $C = \mathrm{Ca} + \mathrm{Na} + \mathrm{K} - \overline{\mathrm{Ca} + \mathrm{Na} + \mathrm{K}}$, $\Gamma = \gamma - \bar{\gamma}$, $\mathrm{B} = \beta - \bar{\beta}$, $\mathrm{A} = \alpha - \bar{\alpha}$ where the bar indicates a mean.

| No. | $S \times 10^2$. | $T \times 10^2$. | $F \times 10^2$. | $M \times 10^2$. | $C \times 10^2$. | $\Gamma \times 10^4$. | $\mathrm{B} \times 10^4$. | $\mathrm{A} \times 10^4$. |
|---|---|---|---|---|---|---|---|---|
| 1 | −104 | 1 | 45 | −117 | 25 | 204 | 193 | 169 |
| 8 | −74 | 21 | 5 | −76 | −8 | 141 | 153 | 156 |
| 9 | −64 | −2 | 30 | −61 | −4 | 118 | 126 | 123 |
| 14 | −42 | 3 | −7 | −20 | −14 | 42 | 68 | 79 |
| 17 | −23 | 14 | 33 | −87 | 13 | 94 | 118 | 143 |
| 22 | 53 | 5 | 70 | −45 | −12 | 28 | 13 | 56 |
| 26 | 59 | 1 | 7 | 29 | −8 | −60 | −93 | −68 |
| 29 | 61 | −14 | −78 | 141 | 21 | −227 | −207 | −217 |
| 30 | 60 | −14 | −51 | 97 | 0 | −167 | −197 | −235 |
| 35 | 72 | −14 | −56 | 137 | −13 | −173 | −176 | −209 |

table I; it will usually be sufficient if the several means are taken to the same number of decimal places as the quantities being averaged. Next, all the variables are expressed in the form of differences from their respective means, as in tables IIA and IIB.

[1] That is, differences between the observed optical data and the values calculated from the regression equation.

TABLE IIB. X-ray data for analysed specimens of anthophyllite, expressed as differences from the means ($M_x$) of table I, together with the squares and products required for the derivation of a regression equation, and the calculated values and residuals obtained from the resulting equation. $X = b - \bar{b}$; $\hat{X}$ is the calculated value of $X$; other symbols as in table I.

| No. | $S\times10^2$. | $F\times10^2$. | $M\times10^2$. | $C\times10^2$. | $X\times10^2$. | $S^2\times10^4$. | $SF\times10^4$. | $SM\times10^4$. | $SC\times10^4$. | $F^2\times10^4$. | $FM\times10^4$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | −98 | 59 | −104 | 23 | 1 | 9604 | −5782 | 10192 | −2254 | 3481 | −6136 |
| 8 | −68 | 19 | −63 | −11 | −9 | 4624 | −1292 | 4284 | 748 | 361 | −1197 |
| 9 | −58 | 44 | −48 | −7 | −11 | 3364 | −2552 | 2784 | 406 | 1936 | −2112 |
| 14 | −36 | 7 | −7 | −17 | −25 | 1296 | −252 | 252 | 612 | 49 | −49 |
| 17 | −17 | 47 | −70 | 10 | 4 | 289 | −799 | 1190 | −170 | 2209 | −3290 |
| 20 | 24 | 38 | −174 | −19 | 19 | 576 | 912 | −4176 | −456 | 1444 | −6612 |
| 26 | 65 | 21 | 42 | −11 | 13 | 4225 | 1365 | 2730 | −715 | 441 | 882 |
| 29 | 67 | −64 | 154 | 18 | −1 | 4489 | −4288 | 10318 | 1206 | 4096 | 9856 |
| 30 | 66 | −37 | 110 | −3 | 7 | 4356 | −2442 | 7260 | −198 | 1369 | −4070 |
| 43 | 58 | −132 | 163 | 12 | −1 | 3364 | −7656 | 9454 | 696 | 17424 | −21516 |
| Σ | — | - | — | — | - | 36187 | −22786 | 44288 | −125 | 32810 | −53956 |

| No. | $FC\times10^4$. | $M^2\times10^4$. | $MC\times10^4$. | $C^2\times10^4$. | $XS\times10^4$. | $XF\times10^4$. | $XM\times10^4$. | $XC\times10^4$. | $X^2\times10^4$. | $\hat{X}\times10^2$. | $(X-\hat{X})\times10^2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1359 | 10816 | −2392 | 529 | −98 | 59 | −104 | 23 | 1 | −5 | 6 |
| 8 | −209 | 3969 | 693 | 121 | 612 | −171 | 567 | 99 | 81 | −15 | 6 |
| 9 | −308 | 2304 | 336 | 49 | 638 | −484 | 528 | 77 | 121 | −13 | 2 |
| 14 | −119 | 49 | 119 | 289 | 900 | −175 | 175 | 425 | 625 | −16 | −9 |
| 17 | 470 | 4900 | −700 | 100 | −68 | 188 | −280 | 40 | 16 | 8 | −4 |
| 20 | −722 | 30276 | 3306 | 361 | 456 | 722 | −3306 | −361 | 361 | 22 | −3 |
| 26 | −231 | 1764 | −462 | 121 | 845 | 273 | 546 | −143 | 169 | 8 | 5 |
| 29 | −1152 | 23716 | 2772 | 324 | −67 | 64 | −154 | −18 | 1 | 5 | −6 |
| 30 | 111 | 12100 | −330 | 9 | 462 | −259 | 770 | −21 | 49 | 3 | 4 |
| 43 | −1584 | 26569 | 1956 | 144 | −58 | 132 | −163 | −12 | 1 | 0 | −1 |
| Σ | −2385 | 116463 | 5298 | 2047 | 3622 | 349 | −1421 | 109 | 1425 | — | — |

Now in the general case we may have $N$ sets of observations, each set referring to $m$ specified physical properties ($X$, $Y$, $Z$,....) which are dependent variables and each of which is to be correlated with $n$ independent variables such as the parameters of composition ($A$, $B$, $C$,...; or in practice $SiO_2$, $Al_2O_3$, &c.). And all these variables have been expressed in the form of differences from their respective means. We can therefore set up for each physical quantity $N$ equations of the type:[1]

$$X_i = a_x A_i + b_x B_i + c_x C_i ... + p_x P_i \ (i = 1,2,..., N),$$

where $a_x$, $b_x$, $c_x$,... are constants, $n$ in number.

Considering in the first place only the $N$ equations for the one physical quantity $X$, the squares of the coefficients $A_i$, $B_i$, $C_i$,... and their products in pairs $A_iB_i$, $A_iC_i$, $A_iD_i$,..., $B_iC_i$, $B_iD_i$,..., $C_iD_i$,... are evaluated and tabulated as in table IIB (there will be $n(n+1)/2$ such terms). The products $X_iA_i$, $X_iB_i$, $X_iC_i$,... are also calculated ($n$ terms). Corresponding products are now summed over the $N$ equations, and from the sums a matrix equation in $a_x$, $b_x$, $c_x$,... can be set up:

$$\begin{Vmatrix} \sum A_i^2 & \sum A_iB_i & \sum A_iC_i & \dots & \sum A_iP_i \\ \sum A_iB_i & \sum B_i^2 & \sum B_iC_i & \dots & \sum B_iP_i \\ \sum A_iC_i & \sum B_iC_i & \sum C_i^2 & \dots & \sum C_iP_i \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \sum A_iP_i & \sum B_iP_i & \sum C_iP_i & \dots & \sum P_i^2 \end{Vmatrix} \cdot \begin{Vmatrix} a_x \\ b_x \\ c_x \\ \cdot \\ \cdot \\ \cdot \\ P_x \end{Vmatrix} = \begin{Vmatrix} \sum X_iA_i \\ \sum X_iB_i \\ \sum X_iC_i \\ \cdot \\ \cdot \\ \cdot \\ \sum X_iP_i \end{Vmatrix} \ (i = 1,2,3,..., N).$$

A similar equation can be set up for each of the other physical

[1] It will be noticed that the equations are homogeneous, containing no constant term. In general, a regression equation correlating one dependent variable with $n$ independent variables will contain a constant term, making $n+1$ constants, and in the derivation of the equation determinants of order $n+1$ will be involved. But if all the variables are expressed as differences from the mean, the constant term becomes zero. For if we assume that the constant term is $\zeta_x$, we have $X_i = \zeta_x + a_xA_i + b_xB_i + c_xC_i + ...$; and summing, $\sum X_i = N\zeta_x + a_x \sum A_i + b_x \sum B_i + c_x \sum C_i + ...$ ($i = 1,2,..., N$); but if $X_i$, $A_i$, &c. are measured from their several means, the sums $\sum X_i$, $\sum A_i$,... are all zero; hence $\zeta_x = 0$. This elimination of the constant term reduces the order of the determinants involved in the derivation of the regression equations from $n+1$ to $n$, which amply repays the labour of expressing all the variables as differences from their means. It will also be obvious that if the number of sets of observations, $N$, is less than the number of independent variables, $n$, the system of $N$ equations has no definite solution; if $N = n$ a solution is possible; and if, as will normally be the case, $N > n$, the equations will form an inconsistent system, from which, however, an optimum solution can be derived by the method of least squares; in what follows, we assume that $N > n$ and apply the method of least squares.

quantities, $Y$, $Z$,...; but provided[1] that all the physical quantities relate to the same $N$ sets of values of the independent variables $A$, $B$, $C$,..., the left-hand matrix will be the same in all the equations, which can therefore all be combined into a single equation:

$$\left\|\begin{matrix} \Sigma A_i^2 & \Sigma A_iB_i & \Sigma A_iC_i \dots & \Sigma A_iP_i \\ \Sigma A_iB_i & \Sigma B_i^2 & \Sigma B_iC_i \dots & \Sigma B_iP_i \\ \Sigma A_iC_i & \Sigma B_iC_i & \Sigma C^2 \dots & \Sigma C_iP_i \\ \cdot & \cdot & \cdot \dots & \cdot \\ \cdot & \cdot & \cdot \dots & \cdot \\ \cdot & \cdot & \cdot \dots & \cdot \\ \Sigma A_iP_i & \Sigma B_iP_i & \Sigma C_iP_i \dots & \Sigma P_i^2 \end{matrix}\right\| \cdot \left\|\begin{matrix} a_x & a_y & a_z \dots \\ b_x & b_y & b_z \dots \\ c_x & c_y & c_z \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ p_x & p_y & p_z \dots \end{matrix}\right\| = \left\|\begin{matrix} \Sigma X_iA_i & \Sigma Y_iA_i & \Sigma Z_iA_i \dots \\ \Sigma X_iB_i & \Sigma Y_iB_i & \Sigma Z_iB_i \dots \\ \Sigma X_iC_i & \Sigma Y_iC_i & \Sigma Z_iC_i \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \Sigma X_iP_i & \Sigma Y_iP_i & \Sigma Z_iP_i \dots \end{matrix}\right\|.$$

In this equation, it will be seen that the left-hand matrix (which is a symmetrical square matrix of order $n \times n$) contains only the sums of squares and products of the independent variables; the central matrix contains all the desired coefficients of the regression equations; and the dependent variables, the $m$ quantities $X$, $Y$, $Z$,..., only occur in the right-hand matrix; the central and right-hand matrices are both of order $n \times m$.

To solve the equation (that is, to evaluate the central matrix of unknown constants), the most satisfactory procedure is to premultiply the right-hand matrix by the covariance matrix, which is the reciprocal of the left-hand matrix and, like it, is a symmetrical square matrix of order $n \times n$. To evaluate the covariance matrix, we must solve the equation:

$$\left\|\begin{matrix} \Sigma A_i^2 & \Sigma A_iB_i & \Sigma A_iC_i & \dots & \Sigma A_iP_i \\ \Sigma A_iB_i & \Sigma B_i^2 & \Sigma B_iC_i & \dots & \Sigma B_iP_i \\ \Sigma A_iC_i & \Sigma B_iC_i & \Sigma C_i^2 & \dots & \Sigma C_iP_i \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \Sigma A_iP_i & \Sigma B_iP_i & \Sigma C_iP_i & \dots & \Sigma P_i^2 \end{matrix}\right\| \cdot \left\|\begin{matrix} \xi_{11} & \xi_{12} & \xi_{13} & \dots & \xi_{1p} \\ \xi_{21} & \xi_{22} & \xi_{23} & \dots & \xi_{2p} \\ \xi_{31} & \xi_{32} & \xi_{33} & \dots & \xi_{3p} \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \xi_{p1} & \xi_{p2} & \xi_{p3} & \dots & \xi_{pp} \end{matrix}\right\| = \left\|\begin{matrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ 0 & 0 & 0 & \dots & 1 \end{matrix}\right\|.$$

The solution of this equation is $\xi_{ij} = D_{ij}/D_0$, where $\xi_{ij}$ is the element appearing in the $i$th row and $j$th column of the covariance matrix, $D_0$ is the determinant of the left-hand matrix (the matrix of sum of squares and products of the independent variables), and $D_{ij}$ is the determinant obtained by replacing the $i$th column of $D_0$ by the $j$th column of the right-hand unit matrix.

[1] This proviso will usually have been met during the preliminary selection and preparation of the data. If for any reason a different group of independent variables must be used for any particular physical quantity, the whole procedure, including the preparatory expression of the data as differences from their means, will have to be carried out separately for that physical quantity. This is exemplified in the case of anthophyllite by the data for the unit-cell dimension, $b$ (tables I and IIB; compare table IIA).

A systematic procedure for the evaluation of the covariance matrix will be considered below; for the moment, we will assume that it has been evaluated. Then we can write:

$$\begin{Vmatrix} a_x & a_y & a_z \dots \\ b_x & b_y & b_z \dots \\ c_x & c_y & c_z \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ p_x & p_y & p_z \dots \end{Vmatrix} = \begin{Vmatrix} \xi_{11} & \xi_{12} & \xi_{13} & \dots & \xi_{1p} \\ \xi_{21} & \xi_{22} & \xi_{23} & \dots & \xi_{2p} \\ \xi_{31} & \xi_{32} & \xi_{33} & \dots & \xi_{3p} \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \xi_{p1} & \xi_{p2} & \xi_{p3} & \dots & \xi_{pp} \end{Vmatrix} \cdot \begin{Vmatrix} \sum X_i A_i & \sum Y_i A_i & \sum Z_i A_i \dots \\ \sum X_i B_i & \sum Y_i B_i & \sum Z_i B_i \dots \\ \sum X_i C_i & \sum Y_i C_i & \sum Z_i C_i \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \cdot & \cdot & \cdot \dots \\ \sum X_i P_i & \sum Y_i P_i & \sum Z_i P_i \dots \end{Vmatrix}.$$

Multiplying out, any element of the left-hand matrix of regression coefficients, say that in the $i$th row and $j$th column, is obtained by multiplying the several elements of the corresponding column (the $j$th) of the right-hand matrix by the elements of the corresponding row (the $i$th) of the covariance matrix and adding the products. Thus in the second row and third column:

$$b_z = \xi_{21} \sum Z_i A_i + \xi_{22} \cdot \sum Z_i B_i + \xi_{23} \cdot \sum Z_i C_i + \dots + \xi_{2p} \cdot \sum Z_i P_i.$$

Finally, we arrive at the desired regression equations:

$$\hat{X}_i = A_i a_x + B_i b_x + C_i c_x + \dots + P_i p_x \pm \hat{\sigma}_x;$$

$$\hat{Y}_i = A_i a_y + B_i b_y + C_i c_y + \dots + P_i p_y \pm \hat{\sigma}_y;$$

&c., or in matrix form:

$$\begin{Vmatrix} \hat{X}_i \\ \hat{Y}_i \\ \hat{Z}_i \\ \cdot \\ \cdot \end{Vmatrix} = \begin{Vmatrix} a_x & b_x & c_x & \dots & p_x \\ a_y & b_y & c_y & \dots & p_y \\ a_z & b_z & c_z & \dots & p_z \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \end{Vmatrix} \cdot \begin{Vmatrix} A_i \\ B_i \\ C_i \\ \cdot \\ \cdot \\ P_i \end{Vmatrix} \pm \begin{Vmatrix} \hat{\sigma}_x \\ \hat{\sigma}_y \\ \hat{\sigma}_z \\ \cdot \\ \cdot \end{Vmatrix}.$$

It will be noticed that $\hat{X}_i$, $\hat{Y}_i$, &c., are used for the estimated values of the dependent variables, derived from the regression equations, and that each equation includes a standard deviation term, $\hat{\sigma}_x$, $\hat{\sigma}_y$, &c. The standard deviation terms may be derived in two ways, and it may be thought desirable to use both as a check, though exact agreement will not normally be obtained on account of the approximations used in the course of the calculations. One procedure is to compare the observed and estimated values of the dependent variables, forming the residuals

$X_i - \hat{X}_i$, $Y_i - \hat{Y}_i$, &c.; then $\hat{\sigma}_x^2 = \sum (X_i - \hat{X}_i)^2/N$, &c. The other procedure is to use the relation

$$N\hat{\sigma}_x^2 = \sum X_i^2 - a_x \sum X_i A_i - b_x \sum X_i B_i - c_x \sum X_i C_i - \ldots - p_x \sum X_i P_i.$$

For our example of anthophyllite, it would take too much space to follow through the derivation of the regression equations for all the dependent variables in full detail, but the first stage of the procedure for the cell-side $b$ is illustrated in table IIB; the sums of squares and products in this table, and the corresponding sums for table IIA (the derivation of which is not shown) lead to the two matrix equations:

$$\begin{Vmatrix} 3{\cdot}6187 & -2{\cdot}2786 & 4{\cdot}4288 & -0{\cdot}0125 \\ -2{\cdot}2786 & 3{\cdot}2810 & -5{\cdot}3956 & -0{\cdot}2385 \\ 4{\cdot}4288 & -5{\cdot}3956 & 11{\cdot}6463 & 0{\cdot}5298 \\ -0{\cdot}0125 & -0{\cdot}2385 & 0{\cdot}5298 & 0{\cdot}2047 \end{Vmatrix} \cdot \begin{Vmatrix} s_x \\ f_x \\ m_x \\ c_x \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}3622 \\ 0{\cdot}0349 \\ 0{\cdot}1421 \\ 0{\cdot}0109 \end{Vmatrix}, \text{ and}$$

$$\times 10^2$$

$$\begin{Vmatrix} 4{\cdot}1476 & -0{\cdot}4356 & -1{\cdot}5162 & 4{\cdot}8148 & -0{\cdot}2226 \\ -0{\cdot}4356 & 0{\cdot}1265 & 0{\cdot}3478 & -0{\cdot}8315 & -0{\cdot}0175 \\ -1{\cdot}5162 & 0{\cdot}3478 & 2{\cdot}0858 & -3{\cdot}6770 & -0{\cdot}0314 \\ 4{\cdot}8148 & -0{\cdot}8315 & -3{\cdot}6770 & 8{\cdot}2080 & -0{\cdot}1436 \\ -0{\cdot}2226 & -0{\cdot}0175 & -0{\cdot}0314 & -0{\cdot}1436 & 0{\cdot}1888 \end{Vmatrix} \cdot \begin{Vmatrix} s_\Gamma & s_B & s_A \\ t_\Gamma & t_B & t_A \\ f_\Gamma & f_B & f_A \\ m_\Gamma & m_B & m_A \\ c_\Gamma & c_B & c_A \end{Vmatrix} = \begin{Vmatrix} -8{\cdot}1507 & -8{\cdot}6495 & -8{\cdot}6471 \\ 1{\cdot}2389 & 1{\cdot}3102 & 1{\cdot}4811 \\ 5{\cdot}3684 & 5{\cdot}2956 & 5{\cdot}9468 \\ -12{\cdot}5707 & -12{\cdot}9211 & -13{\cdot}8756 \\ 0{\cdot}1760 & 0{\cdot}2208 & 0{\cdot}1167 \end{Vmatrix}$$

In both these equations the coefficients $s_x$, $s_\Gamma$, $s_B$, $s_A$ are the coefficients of $S$ in the desired regression equations for $X$, $\Gamma$, B, and A respectively (these symbols are defined in tables I and II), while $t$, $f$, $m$, and $c$ are the corresponding coefficients of $T$, $F$, $M$, and $C$; and the power of 10 written over the first term of a matrix is to be understood, here and later, as multiplying every term of the matrix.

The two covariance matrices, which are the reciprocals of the left-hand matrices of these two equations, are next found by the procedure outlined below (p. 93):

$$\begin{Vmatrix} \xi_{ss} & \xi_{sf} & \xi_{sm} & \xi_{sc} \\ \xi_{fs} & \xi_{ff} & \xi_{fm} & \xi_{fc} \\ \xi_{ms} & \xi_{mf} & \xi_{mm} & \xi_{mc} \\ \xi_{cs} & \xi_{cf} & \xi_{cm} & \xi_{cc} \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}6759 & 0{\cdot}1898 & -0{\cdot}1875 & 0{\cdot}7248 \\ 0{\cdot}1898 & 1{\cdot}2858 & 0{\cdot}5423 & 0{\cdot}1558 \\ -0{\cdot}1875 & 0{\cdot}5423 & 0{\cdot}4276 & -0{\cdot}4945 \\ 0{\cdot}7248 & 0{\cdot}1556 & -0{\cdot}4945 & 6{\cdot}3390 \end{Vmatrix} \text{ (for } X\text{) and}$$

$$\begin{Vmatrix} \xi_{ss} & \xi_{st} & \xi_{sf} & \xi_{sm} & \xi_{sc} \\ \xi_{ts} & \xi_{tt} & \xi_{tf} & \xi_{tm} & \xi_{tc} \\ \xi_{fs} & \xi_{ft} & \xi_{ff} & \xi_{fm} & \xi_{fc} \\ \xi_{ms} & \xi_{mt} & \xi_{mf} & \xi_{mm} & \xi_{mc} \\ \xi_{cs} & \xi_{ct} & \xi_{cf} & \xi_{cm} & \xi_{cc} \end{Vmatrix} = \begin{Vmatrix} 6{\cdot}891 & -18{\cdot}836 & -12{\cdot}072 & -11{\cdot}434 & -4{\cdot}325 \\ -18{\cdot}836 & 82{\cdot}349 & 36{\cdot}260 & 35{\cdot}962 & 18{\cdot}808 \\ -12{\cdot}072 & 36{\cdot}260 & 24{\cdot}058 & 21{\cdot}699 & 9{\cdot}634 \\ -11{\cdot}434 & 35{\cdot}962 & 21{\cdot}699 & 20{\cdot}348 & 8{\cdot}939 \\ -4{\cdot}325 & 18{\cdot}808 & 9{\cdot}634 & 8{\cdot}939 & 10{\cdot}342 \end{Vmatrix} \text{ (for } \Gamma\text{, B, and A).}$$

Applying the covariance matrix for $X$:

$$\begin{Vmatrix} s_x \\ f_x \\ m_x \\ c_x \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}6759 & 0{\cdot}1898 & -0{\cdot}1875 & 0{\cdot}7248 \\ 0{\cdot}1898 & 1{\cdot}2858 & 0{\cdot}5423 & 0{\cdot}1558 \\ -0{\cdot}1875 & 0{\cdot}5423 & 0{\cdot}4276 & -0{\cdot}4945 \\ 0{\cdot}7248 & 0{\cdot}1558 & -0{\cdot}4945 & 6{\cdot}3390 \end{Vmatrix} \cdot \begin{Vmatrix} 0{\cdot}3622 \\ 0{\cdot}0349 \\ -0{\cdot}1421 \\ 0{\cdot}0109 \end{Vmatrix}$$

$$= \begin{Vmatrix} 0{\cdot}6759 \times 0{\cdot}3622 + 0{\cdot}1898 \times 0{\cdot}0349 + 0{\cdot}1875 \times 0{\cdot}1421 + 0{\cdot}7248 \times 0{\cdot}0109 \\ 0{\cdot}1898 \times 0{\cdot}3622 + 1{\cdot}2858 \times 0{\cdot}0349 - 0{\cdot}5423 \times 0{\cdot}1421 + 0{\cdot}1558 \times 0{\cdot}0109 \\ -0{\cdot}1875 \times 0{\cdot}3622 + 0{\cdot}5423 \times 0{\cdot}0349 - 0{\cdot}4276 \times 0{\cdot}1421 - 0{\cdot}4945 \times 0{\cdot}0109 \\ 0{\cdot}7248 \times 0{\cdot}3622 + 0{\cdot}1558 \times 0{\cdot}0349 + 0{\cdot}4945 \times 0{\cdot}1421 + 6{\cdot}3390 \times 0{\cdot}0109 \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}286 \\ 0{\cdot}038 \\ -0{\cdot}115 \\ 0{\cdot}407 \end{Vmatrix}.$$

Hence we derive the regression equation for $X$:

$$\hat{X} = 0{\cdot}286\,S + 0{\cdot}038\,F - 0{\cdot}115\,M + 0{\cdot}407\,C,$$

with a variance

$$\begin{aligned}\hat{\sigma}_x^2 &= (\Sigma X^2 - s_x \Sigma XS - f_x \Sigma XF - m_x \Sigma XM - c_x \Sigma XC)/N \\ &= (0{\cdot}1425 - 0{\cdot}286 \times 0{\cdot}3622 - 0{\cdot}038 \times 0{\cdot}0349 - 0{\cdot}115 \times 0{\cdot}1421 - \\ &\qquad - 0{\cdot}407 \times 0{\cdot}0109)/10 \\ &= 0{\cdot}0017,\end{aligned}$$

and standard deviation $\hat{\sigma}_x = 0{\cdot}04$. Lastly, we replace the differences from the mean, $S$, $F$, $M$, $C$, and $X$, by the measured quantities Si, Fe″+Mn, Mg, Ca+Na+K, and $b$, arriving at the final form of our regression equation for $b$:

$$\begin{aligned}\hat{b} - 17{\cdot}95 &= 0{\cdot}286\ (\mathrm{Si} - 7{\cdot}18) + 0{\cdot}038\ (\mathrm{Fe''} + \mathrm{Mn} - 1{\cdot}64) - \\ &\quad - 0{\cdot}165\ (\mathrm{Mg} - 4{\cdot}41) + 0{\cdot}407\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K} - 0{\cdot}19) \pm 0{\cdot}04, \\ \hat{b} &= 16{\cdot}48 + 0{\cdot}286\ \mathrm{Si} + 0{\cdot}038\ (\mathrm{Fe''} + \mathrm{Mn}) - 0{\cdot}165\ \mathrm{Mg} + \\ &\quad + 0{\cdot}407\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}04.\end{aligned}$$

Similarly, we arrive at regression equations for $\gamma$, $\beta$, and $\alpha$:

$$\begin{aligned}\hat{\gamma} &= 1{\cdot}7273 - 0{\cdot}0134\ \mathrm{Si} + 0{\cdot}0145\ (\mathrm{Ti} + \mathrm{Fe'''}) + 0{\cdot}0140\ (\mathrm{Fe''} + \mathrm{Mn}) + \\ &\quad + 0{\cdot}0002\ \mathrm{Mg} - 0{\cdot}0030\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}0009, \\ \hat{\beta} &= 1{\cdot}7299 - 0{\cdot}0143\ \mathrm{Si} + 0{\cdot}0232\ (\mathrm{Ti} + \mathrm{Fe'''}) + 0{\cdot}0108\ (\mathrm{Fe''} + \mathrm{Mn}) - \\ &\quad - 0{\cdot}0002\ \mathrm{Mg} - 0{\cdot}0015\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}0014, \\ \hat{\alpha} &= 1{\cdot}7009 - 0{\cdot}0113\ \mathrm{Si} + 0{\cdot}0368\ (\mathrm{Ti} + \mathrm{Fe'''}) + 0{\cdot}0120\ (\mathrm{Fe''} + \mathrm{Mn}) - \\ &\quad - 0{\cdot}0012\ \mathrm{Mg} - 0{\cdot}0028\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}0021.\end{aligned}$$

This completes the derivation of the desired regression equations. But we notice that they contain several very small coefficients, and we may reasonably doubt whether these differ significantly from zero. It is not difficult to test whether this is so, to test whether two coefficients that are nearly equal differ significantly from one another, and to decide how many significant figures are justifiable in each coefficient.

*The standard deviations of the regression coefficients; tests of the significance of the regression coefficients.*

An estimate of the standard deviations of the regression coefficients can very readily be made by using the covariance matrix. For if the estimated standard deviation of the dependent variable, $X$, is $\hat{\sigma}_x$, and

the estimated standard deviations of the regression coefficients $a_x$, $b_x$, $c_x$,... are $\hat{\sigma}_{x,a}$, $\hat{\sigma}_{x,b}$, &c., then $\hat{\sigma}^2_{x,a} = \sigma^2_x \xi_{11}\, N/(N-n-1)$, where $N$ is the number of observed values of $X$ and $n$ the number of independent variables $a$, $b$, &c.; or in general for the $k$th in the series $\hat{\sigma}_{x,a}$, $\hat{\sigma}_{x,b}$,..., we have $\hat{\sigma}^2_{x,k} = \hat{\sigma}^2_x \xi_{kk} N/(N-n-1)$.

For the coefficients of the regression equation derived above for the $b$ cell-dimension of anthophyllite, we have:

$$\hat{\sigma}^2_{b,s} = \hat{\sigma}^2_b \xi_{ss} N/(N-n-1) = 0{\cdot}0017 \times 0{\cdot}6759 \times 10/5 = 0{\cdot}0023;$$
$$\hat{\sigma}^2_{b,f} = 0{\cdot}0017 \times 1{\cdot}2858 \times 10/5 = 0{\cdot}0044;$$
$$\hat{\sigma}^2_{b,m} = 0{\cdot}0017 \times 0{\cdot}4276 \times 10/5 = 0{\cdot}0014;$$
$$\hat{\sigma}^2_{b,c} = 0{\cdot}0017 \times 6{\cdot}3390 \times 10/5 = 0{\cdot}0215$$

(note that the second factor in each is an element of the principal diagonal of the covariance matrix). Hence we have

$$\hat{\sigma}_{b,s} = 0{\cdot}048, \quad \hat{\sigma}_{b,f} = 0{\cdot}066, \quad \hat{\sigma}_{b,m} = 0{\cdot}037, \quad \hat{\sigma}_{b,c} = 0{\cdot}147,$$

and

$$s_b = 0{\cdot}286 \pm 0{\cdot}048, \quad f_b = 0{\cdot}038 \pm 0{\cdot}066, \quad m_b = -0{\cdot}115 \pm 0{\cdot}037,$$
$$c_b = 0{\cdot}407 \pm 0{\cdot}147.$$

It is obvious that the coefficient $f_b$, with a standard deviation much greater than the coefficient itself, is not significantly different from zero; but some quantitative test for the significance of the coefficients is desirable, and is, in fact, readily available. Most collections of tabulated statistical functions include a table of 'Student's ratio', $t$. This is the ratio of a quantity to its standard deviation, and the tabulated figures are the probabilities, for given values of Student's ratio and given numbers of degrees of freedom, that the quantity under consideration does not differ significantly from zero. It is not necessary for our purpose to consider the exact meaning of the term 'degrees of freedom' in statistical theory; it will suffice to say that in this connexion the number of degrees of freedom is $N-n-1$: $N$ and $n$ are defined above.[1] Applying this procedure to our example, the values of Student's ratio are

$$t_{b,s} = s_b/\hat{\sigma}_{b,s} = 6{\cdot}0, \quad t_{b,f} = 0{\cdot}57, \quad t_{b,m} = 3{\cdot}1, \quad t_{b,c} = 2{\cdot}8,$$

and there are 5 degrees of freedom; from the tables the corresponding

[1] In this connexion, it must not be forgotten that $n$ is the number of independent variables *remaining*, not necessarily the original number the investigation started with; if any terms have been rejected from the regression equation as not significantly different from zero, $n$ will be reduced accordingly.

probabilities that the several coefficients are not significantly different from zero are $P_{b,s} < 0{\cdot}01$, $P_{b,f}$ 0·6, $P_{b,m}$ 0·03, $P_{b,c}$ 0·04. The degree of probability that a coefficient is significantly different from zero is of course a matter for the judgement of the individual worker, but this simple technique does provide an objective measure of that probability. We have accepted a probability of 0·40 or less as justifying the inclusion of the term in question, and on this basis the term in $F$ may be rejected from the equation for $b$ as not justified by the data at present available, while the terms in $S$, $M$, and $C$ must be retained.[1] This does not imply that $b$ does not vary with Fe″+Mn, but merely that the data at present available are not adequate to prove any such variation.

When any coefficient of a regression equation has been shown not to differ significantly from zero, we proceed to eliminate that term and readjust the remaining coefficients to give the best representation of the observations. But before considering the procedure for this readjustment it is desirable to consider the possibility that two coefficients may not differ significantly from one another, when it would be proper to replace the two separate terms in two independent variables, say $B$ and $G$, by a single term in their sum, $B+G$, adjusting all the coefficients accordingly.

To test whether two coefficients, say $b_x$ and $g_x$, differ significantly from one another, we divide their difference by its standard deviation to obtain the appropriate Student's ratio $t_{x,b-g}$; then from the tables, with this value of $t$ and $N-n-1$ degrees of freedom, we derive the probability $P_{x,b-g}$ that the two coefficients do not differ significantly from one another. The standard deviation $\hat{\sigma}_{x,b-g}$ of the difference $b-g$ is given, in terms of the standard deviation $\hat{\sigma}_x$ of the dependent variable, by the relation: $\hat{\sigma}^2_{x,b-g} = \hat{\sigma}^2_x(\xi_{22}+\xi_{77}-2\xi_{27})\,N/(N-n-1)$; the appropriate elements of the covariance matrix are $\xi_{22}$, $\xi_{77}$, and $\xi_{27}$ because $b$ and $g$ are second and seventh in the series $a$, $b$, $c$,....

Considering the remaining, adjusted coefficients of the regression equation for the $b$ cell-dimension of anthophyllite, after elimination of $f_b$ (see p. 84) it is obvious that since all the coefficients have been shown to differ significantly from zero, the negative coefficient $m_b = -0{\cdot}131$ must differ significantly from the two positive coefficients $s_b = 0{\cdot}280$ and $c_b = 0{\cdot}403$. The difference of the two positive coefficients, $c_b - s_b$,

[1] An alternative test, less rigorously based but quite adequate for most investigations, is to accept any coefficient as probably significant if it is greater than its standard deviation. This test has the advantage of not requiring tables of Student's ratio.

is 0·123, and the standard variation of this difference is given by:

$$\begin{aligned}\hat{\sigma}^2_{b,c-s} &= \hat{\sigma}_b(\xi_{cc}+\xi_{ss}-2\xi_{cs})N/(N-n-1)\\ &= 0{\cdot}00181\ (0{\cdot}6479+6{\cdot}3201-2\times 0{\cdot}7018)\ 10/(10-3-1)\\ &= 0{\cdot}0168,\end{aligned}$$

whence $\hat{\sigma}_{b,c-s} = 0{\cdot}130$; then $t_{c-s} = (c-s)/\hat{\sigma}_{b,c-s} = 0{\cdot}123/0{\cdot}130 = 0{\cdot}95$, and with six degrees of freedom, we find from the tables $P_{b,c-s} = 0{\cdot}38$; this is on the borderline of significance, but we retain the separate terms because of the chemical contrast between the independent variables involved, Si and Ca+Na+K.

*Procedure for the elimination of a non-significant term from the regression equations.*

If it has been established that one of the coefficients, say the $k$th in the series $a$, $b$, $c$,..., does not differ significantly from zero, it can be eliminated, and the remaining coefficients adjusted by recalculating a new covariance matrix of reduced order $(n-1)$; the general term, $\xi'_{ij}$, of the new matrix is derived from the corresponding term, $\xi_{ij}$, of the old (not counting the $k$th row and column of the old matrix) by the relation

$$\xi'_{ij} = \xi_{ij} - \xi_{ik}\cdot\xi_{jk}/\xi_{kk}.$$

The matrix of coefficients is then found by postmultiplying the reduced covariance matrix by the matrix of sums and products of the independent variables, excluding the row appropriate to the eliminated independent variable.

Thus with the equations for the refractive indices of anthophyllite, we have originally (omitting the terms below the principal diagonal of the covariance matrix, which may be inserted by symmetry):

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $s_\Gamma$ | $s_B$ | $s_A$ | = | 6·891 | −18·836 | −12·072 | *−11·434* | −4·325 | • | | −8·1507 | −8·6495 | −8·6471 |
| $t_\Gamma$ | $t_B$ | $t_A$ | | | 82·349 | 36·260 | *35·962* | 18·808 | | | 1·2389 | 1·3102 | 1·4811 |
| $f_\Gamma$ | $f_B$ | $f_A$ | | | | 24·058 | *21·699* | 9·634 | | | 5·3684 | 5·2956 | 5·9468 |
| $m_\Gamma$ | $m_B$ | $m_A$ | | | | | *20·348* | *8·939* | | | *−12·5707* | *−12·9211* | *−13·8756* |
| $c_\Gamma$ | $c_B$ | $c_A$ | | | | | | 10·342 | | | 0·1760 | 0·2208 | 0·1167 |

(The last column is multiplied by $\times 10^{-2}$.)

To adjust the coefficients when we eliminate the terms in $M$ we must eliminate the fourth row and fourth column of the covariance matrix (the italicized terms) by the above procedure, and delete the fourth row of

the other two matrices. For the reduced covariance matrix we may write:

$$\|\xi\|_{\text{STFN}} =$$

$$\left\|\begin{array}{lll} 6{\cdot}891-\frac{(11{\cdot}434)^2}{20{\cdot}348} & -18{\cdot}836+\frac{(11{\cdot}434\times 35{\cdot}962)}{20{\cdot}348} & -12{\cdot}072+\frac{(11{\cdot}434\times 21{\cdot}699)}{20{\cdot}348} \\ & 82{\cdot}349-\frac{(35{\cdot}962)^2}{20{\cdot}348} & 36{\cdot}260-\frac{(35{\cdot}962\times 21{\cdot}699)}{20{\cdot}348} \\ & & 24{\cdot}058-\frac{(21{\cdot}699)^2}{20{\cdot}348} \end{array}\right.$$

$$\left.\begin{array}{l} -4{\cdot}325+\frac{(11{\cdot}434\times 8{\cdot}939)}{20{\cdot}348} \\ 18{\cdot}808-\frac{(35{\cdot}962\times 8{\cdot}939)}{20{\cdot}348} \\ 9{\cdot}364-\frac{(21{\cdot}699\times 8{\cdot}939)}{20{\cdot}348} \\ 10{\cdot}342-\frac{(8{\cdot}939)^2}{20{\cdot}348} \end{array}\right\|.$$

The pattern in this expression should be readily apparent. After evaluating it and making a second reduction by the same procedure to eliminate the terms in $c$, which also prove to be non-significant, we arrive at an equation for the remaining coefficients:

$$\left\|\begin{array}{lll} s_\Gamma & s_B & s_A \\ t_\Gamma & t_B & t_A \\ f_\Gamma & f_B & f_A \end{array}\right\| = \left\|\begin{array}{lll} 0{\cdot}3901 & 1{\cdot}0443 & 0{\cdot}1103 \\ & 17{\cdot}3789 & -2{\cdot}1372 \\ & & 0{\cdot}9166 \end{array}\right\| \cdot \left\|\begin{array}{lll} -8{\cdot}1507 & -8{\cdot}6495 & -8{\cdot}6471 \\ 1{\cdot}2389 & 1{\cdot}3102 & 1{\cdot}4811 \\ 5{\cdot}3684 & 5{\cdot}2956 & 5{\cdot}9468 \end{array}\right\| \times 10^{-2}$$

$$= \left\|\begin{array}{lll} -0{\cdot}0129 & -0{\cdot}0142 & -0{\cdot}0117 \\ 0{\cdot}0180 & 0{\cdot}0242 & 0{\cdot}0400 \\ 0{\cdot}0143 & 0{\cdot}0110 & 0{\cdot}0133 \end{array}\right\|.$$

When the new regression equations with these coefficients are tested, it is found that while all the coefficients are significantly different from zero, $t_\Gamma$ and $f_\Gamma$ (0·0180 and 0·0143) are not significantly different from one another. We can therefore compound these terms if we wish, and we now consider how to do so.

*Procedure for compounding two terms of a regression equation whose coefficients do not differ significantly from one another.*

If it has been established that two of the coefficients of a regression equation, say the $k$th and the $q$th of the series $a$, $b$, $c$,..., do not differ significantly from one another, they can be adjusted to equality, and the remaining coefficients adjusted, by recalculating a new covariance matrix of reduced order $(n-1)$. The new, adjusted column and row, replacing the $k$th and the $q$th of the old matrix, can retain the place of either, the other being deleted; if we retain it in the $k$th place, the general term, $\xi'_{ij}$, of the new matrix will be derived from the corresponding term, $\xi_{ij}$, of the old (not counting the $q$th row and $q$th column of the old matrix) by the relation:

$$\xi'_{ij} = \xi_{ij} - (\xi_{ik} - \xi_{iq})(\xi_{jk} - \xi_{jq})/(\xi_{kk} + \xi_{qq} - 2\xi_{kq}),$$

except when $i$ or $j = k$ or $q$; the terms (except $\xi_{kk}$) of the new $k$th row and $k$th column are given by:

$$\xi'_{ik} = (\xi_{ik}+\xi_{iq})-\{\xi_{ik}\xi_{kk}+\xi_{iq}\xi_{qq}-(\xi_{ik}+\xi_{iq})\,\xi_{kq}\}/(\xi_{kk}+\xi_{qq}-2\xi_{kq}),$$

while the new term $\xi'_{kk} = (\xi_{kk}\xi_{qq}-\xi^2_{kq})/(\xi_{kk}+\xi_{qq}-2\xi_{kq})$. The sum of products matrix $\|\sum X_i A_i\|$ will also be modified, the term $\sum X_i K_i$ being replaced by $\sum X_i K_i+\sum X_i Q_i$, and $\sum X_i Q_i$ omitted.

If we apply this procedure[1] to the coefficients of the regression equation for $\Gamma$, two of which ($t_\Gamma$ and $f_\Gamma$) have been found not to differ significantly, we shall start from the equation:

$$\begin{Vmatrix} s_\Gamma \\ t_\Gamma \\ f_\Gamma \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}3901 & 1{\cdot}0443 & 0{\cdot}1103 \\ & 17{\cdot}3789 & -2{\cdot}1372 \\ & & 0{\cdot}9166 \end{Vmatrix} \bullet \begin{Vmatrix} \times 10^{-2} \\ -8{\cdot}1507 \\ 1{\cdot}2389 \\ 5{\cdot}3684 \end{Vmatrix}.$$

The second and third rows (and columns) of the covariance matrix are to be compounded. Only one term of the new matrix, $\xi'_{ss}$, is derived by the first of the above formulae:

$$\xi'_{ss} = 0{\cdot}3901-(1{\cdot}0443-0{\cdot}1103)^2/(17{\cdot}3789+0{\cdot}9166+2\times 2{\cdot}1372)$$
$$= 0{\cdot}3525.$$

The symmetrically equal pair of terms, $\xi'_{st}$ and $\xi'_{ts}$, are derived by the second formula:

$$\xi'_{st} = 1{\cdot}0443+0{\cdot}1103-$$
$$-\{1{\cdot}0443\times 17{\cdot}3789+0{\cdot}1103\times 0{\cdot}9166+2{\cdot}1372\,(1{\cdot}0443+0{\cdot}1103)\}/$$
$$(17{\cdot}3789+0{\cdot}9166+2\times 2{\cdot}1372)$$
$$= 0{\cdot}2365.$$

And the last term is derived by the third formula:

$$\xi'_{tt} = (17{\cdot}3789\times 0{\cdot}9166-2{\cdot}1372^2)/(17{\cdot}3789+0{\cdot}9166+2\times 1{\cdot}1372)$$
$$= 0{\cdot}5026.$$

We now have:

$$\begin{Vmatrix} s_\Gamma \\ (t+f)_\Gamma \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}3525 & 0{\cdot}2365 \\ 0{\cdot}2365 & 0{\cdot}5026 \end{Vmatrix} \bullet \begin{Vmatrix} \times 10^{-2} \\ -8{\cdot}1507 \\ 1{\cdot}2389+5{\cdot}3684 \end{Vmatrix} \quad \begin{matrix} \text{giving } s = 0{\cdot}0130, \\ (t+f) = 0{\cdot}0142. \end{matrix}$$

[1] If the covariance matrix is of low order, as in the present case, it may be simpler to recompute the new matrix from the beginning rather than find it by this process. Referring back to the original matrix of sums of squares and products (the fifth-order square matrix on p. 80), the fourth and fifth columns and fourth and fifth rows, containing $M$ and $C$, are simply suppressed; to write the second and third rows and columns, they are just added together, $\sum A_i(B_i+C_i) = \sum A_iB_i + \sum A_iC_i$, except for the four terms where the second and third columns cross the second and third rows; these four terms $\sum T^2$, $\sum F^2$, and $\sum TF$ (twice) are united by the relation $\sum (T+F)^2 = \sum T^2+\sum F^2+2\sum FT$.

*The regression equations for anthophyllite.*

In the foregoing discussion the selected example, anthophyllite, has been discussed at considerably greater length than will normally be necessary, in order to illustrate the general techniques. For instance, it may often be thought undesirable, or at least unnecessary, to unite two terms of a regression equation whose coefficients are not significantly different; it will often be quite obvious that certain coefficients are not significantly different from zero, without formal calculation of their standard deviations, Student's ratio, and the appropriate probabilities; and when terms are to be deleted or compounded and the coefficients adjusted, it will often be simpler to start anew from a reduced matrix of sums and products rather than to reduce the covariance matrix. But it was felt desirable to set out the procedure for all these operations, since they will sometimes be necessary.

So far as the selected example, anthophyllite, is concerned, we may set out our conclusions in four regression equations,[1] each with its standard deviation; and as a kind of appendix we may add the standard deviations of the several coefficients.[2]

$$\gamma = 1{\cdot}7249 - 0{\cdot}0130\ \mathrm{Si} + 0{\cdot}0140\ (\mathrm{Ti} + \mathrm{Fe}''' + \mathrm{Fe}'' + \mathrm{Mn}) \pm 0{\cdot}0012,$$

$$\beta = 1{\cdot}7275 - 0{\cdot}0142\ \mathrm{Si} + 0{\cdot}024\ (\mathrm{Ti} + \mathrm{Fe}''') + 0{\cdot}0110\ (\mathrm{Fe}'' + \mathrm{Mn}) \pm 0{\cdot}0015,$$

$$\alpha = 1{\cdot}6951 - 0{\cdot}0117\ \mathrm{Si} + 0{\cdot}040\ (\mathrm{Ti} + \mathrm{Fe}''') + 0{\cdot}0133\ (\mathrm{Fe}'' + \mathrm{Mn}) \pm 0{\cdot}0025,$$

$$b(\text{Å.}) = 16{\cdot}44 + 0{\cdot}28\ \mathrm{Si} - 0{\cdot}13\ \mathrm{Mg} + 0{\cdot}40\ (\mathrm{Ca} + \mathrm{Na} + \mathrm{K}) \pm 0{\cdot}04,$$

$$\hat{\sigma}_{\gamma,s} = 0{\cdot}0007, \quad \hat{\sigma}_{\gamma,t} = 0{\cdot}0008, \quad \hat{\sigma}_{\beta,s} = 0{\cdot}0009, \quad \hat{\sigma}_{\beta,t} = 0{\cdot}004,$$

$$\hat{\sigma}_{\beta,f} = 0{\cdot}0015, \quad \hat{\sigma}_{\alpha,s} = 0{\cdot}0015, \quad \hat{\sigma}_{\alpha,t} = 0{\cdot}009, \quad \hat{\sigma}_{\alpha,f} = 0{\cdot}0025,$$

$$\hat{\sigma}_{b,s} = 0{\cdot}05, \quad \hat{\sigma}_{b,m} = 0{\cdot}03, \quad \hat{\sigma}_{b,c} = 0{\cdot}14.$$

It should, perhaps, be emphasized that the standard deviations of the dependent variables ($\gamma$, $\beta$, $\alpha$, and $b$) cannot be taken as a true measure of the accuracy with which the given equations reproduce the true correlation of the physical data with the chemical composition of anthophyllite; they merely measure the accuracy with which the equations reproduce the selected data from which they are derived. It is therefore desirable to compare the whole of the available observations with the calculated values derived from the regression equations.

[1] The $a$ and $c$ cell-dimensions appear to be constant, within the experimental error of the available data.

[2] These serve as an indication of the amounts by which the several coefficients can be varied without gravely upsetting the agreement between observed and calculated values (after appropriate adjustment of the constant term).

Graphs have been prepared in which the residuals (the differences between observed and calculated values) are plotted against each of the five composition parameters, but these do not reveal any evidence of

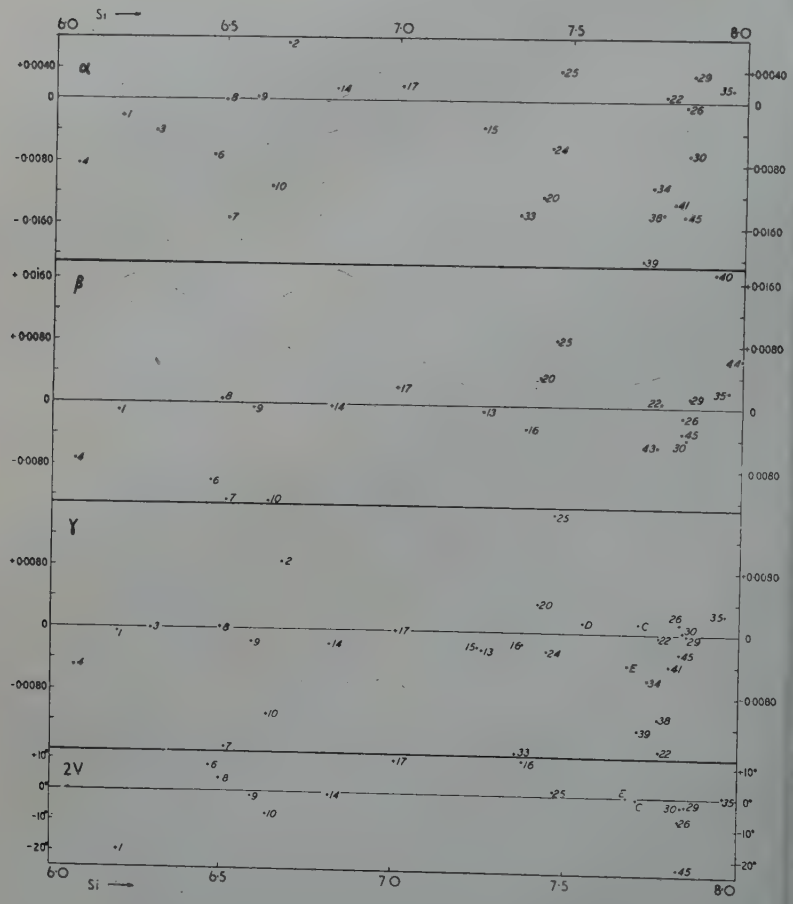


Fig. 1. Departures of the physical properties of anthophyllite from the values calculated from the regression equations, plotted against Si atoms per 24(O,OH,F). The numbers against the points are those used in J. C. Rabbitt's paper; c, d, and e refer to R. Pirani's data.

non-linear variation; one set of these graphs is shown in fig. 1. Graphs of the residuals plotted against the hydroxyl groups per 24(O,OH,F) and against fluorine have been prepared, and suggest that these variables

do not affect the optics, but in view of the limited number[1] of sets of observations and the doubtful accuracy of the chemical data on (OH)′ and F′, conclusions from these graphs must be viewed with great caution; on general grounds, we should expect F′ to lower the refractive indices notably.

On comparison of the observed and calculated refractive indices[2] it is noticeable that (except among the sets of superior data) there is a marked tendency for all three refractive indices to be high or low as a group, relative to the calculated values, rather than for one index to be high and another low (see analyses 6, 7, 10, 25, 33, 38, and 39). This result, which is emphasized by the fact that with only five exceptions (of which three are perhaps doubtful analyses) optic axial angles derived from the regression equations through the calculated refractive indices agree unexpectedly well with the observed values,[3] strongly supports the general accuracy of the regression equations, and suggests that several of the sets of observed refractive indices are subject to a systematic error. Two sets of data, for analyses 38 and 39, are probably low owing to the presence of 1·6 % and 2·4 % of adsorbed water respectively;[4] assuming the mixture law, this should lower their refractive indices by 0·005 and 0·007 respectively; actually, they give values of $\alpha$ 0·012 and 0·016 low, and of $\gamma$ 0·009 and 0·011 low respectively.

There are two sets of data for which the above regression equations do not give satisfactory refractive indices: the Glen Urquhart gedrite and analysis no. 25. The latter is the 'picroamosite' of Serdyuchenko (1936),

[1] Where a large number of observations are available, the neglect of a variable will normally lead to fairly large residuals, which if plotted against the neglected variable will show a distinct trend. But if the neglected variable tends to follow one of those taken into account, its effect will be largely or wholly absorbed by the latter; and if there are only a few observations, false constants will probably be deduced, and the residuals will show only an irregular scatter. It is desirable that there should be at least ten times as many sets of observations as there are variables to be taken into account.

[2] As all the observed data have been published before, and all the calculated data may be derived from the regression equations, it seemed unnecessary to print a table of observed and calculated data, but such a table has been drawn up and deposited in the library of the Mineral Department of the British Museum (Natural History), where it may be consulted, together with a full set of graphs of the residuals plotted against the composition parameters, including OH′ and F′.

[3] The mean difference, excluding the above five analyses, is only 4°, against an expected 10° as calculated from the standard deviations of $\alpha$, $\beta$, and $\gamma$. If the cited 2V(+) for R. Pirani's anthophyllite from Alpe de Brez is a misprint or error for 2V(−), there would be good agreement in this case also.

[4] G. H. Francis and M. H. Hey (in the press).

and has a remarkably high content of $Fe_2O_3$; the disagreement suggests that it may not be an ortho-amphibole, or alternatively that the chemical analysis is in error. For the Glen Urquhart gedrite, we know that the regression equations neglect the variation in total oxygen atoms per unit-cell, which in this material is definitely outside the limits of experimental error; if the observed data for this gedrite are taken, together with the empirical unit-cell contents, to establish approximate additional terms for the effect of extra oxygen ($H_2O$) in the regression equations, we find, approximately:

$$\alpha = \alpha_0 - 0{\cdot}023\ [\Sigma'\ (O,OH,F) - 24];$$

$$\beta = \beta_0 - 0{\cdot}020\ [\Sigma'\ (O,OH,F) - 24];$$

$$\gamma = \gamma_0 - 0{\cdot}016\ [\Sigma'\ (O,OH,F) - 24].$$

Here $\alpha_0$, $\beta_0$, $\gamma_0$ are the values derived from the above incomplete regression equations (but with the composition in terms of one-quarter the empirical unit-cell contents), and $\Sigma'$ (O,OH,F) is expressed for one-quarter the unit-cell contents. If these relations are even approximately true, they suggest that any anthophyllite having interstitial oxygen, as the Glen Urquhart gedrite has, will have strikingly low refractive indices in relation to its composition and should readily be detected by this property.

It may be of interest to note, in general terms, what the above regression equations imply regarding the variations in the cell-dimensions and optical properties of anthophyllite with composition (excluding possible variations in $\Sigma$ (O,OH,F)). The *b*-axis of pure magnesio-anthophyllite should, from the regression equation, be 17·77 Å.; it is lowered by the substitution of $Al_2$ for MgSi, by 0·15 Å. for each MgSi per quarter unit-cell replaced, and raised by the substitution of $Al_2$ for $Mg_3$, by 0·13 Å. for each Mg per quarter unit-cell replaced; substitution of Ca, Na, or K for Mg appears to increase *b* markedly.

Turning to the optical properties, replacement of Mg by Fe″ leads to an increase in all three refractive indices, as usual, hardly any change in $\gamma - \alpha$, and a moderate increase in $\gamma - \beta$, and hence decrease in $2V_\gamma$; for one Fe″ replacing Mg per 24(O,OH,F) the increase is 0·014 for $\gamma$, 0·011 for $\beta$, and 0·013 for $\alpha$. Replacement of MgSi by $Al_2$, in gedrites, leads to an unexpectedly large effect; $Al_2$ replacing MgSi increases $\alpha$ by 0·012, $\beta$ by 0·014, $\gamma$ by 0·013; $\gamma - \alpha$ and $2V_\gamma$ are increased, but $\gamma - \beta$ is decreased. Replacement of Al by Fe‴ or Ti (the data are insufficient to distinguish these) increases the refractive indices markedly. Replace-

ment of Mg by Ca or Na appears to have little effect. Replacement of 3Mg by 2Al also has no noticeable effect.

This work had just been completed when the author received a reprint of a paper by F. Hori,[1] who has applied similar methods to the correlation of the optical properties and chemical composition of the clinopyroxenes; in this group several substitutions that only occur to a minor extent in the anthophyllites go much farther, and it may be of interest to compare the general results of the two studies, though the structures are not so closely related that any close correspondence is to be expected. Hori's equations indicate that a replacement of Mg by Fe″ will increase the refractive indices markedly; for one atom Fe″ replacing Mg per 24 oxygen, the increases will be $\alpha$ 0·014, $\beta$ and $\gamma$ 0·016, a little greater than the effects in anthophyllite. Replacement of MgSi by $Al_2$, again on a comparable basis of 2Al per 24 oxygen, leads to increases in the refractive indices, namely $\alpha$ 0·017, $\beta$ 0·025, $\gamma$ 0·020, again greater effects than in anthophyllite. Replacement of Mg by Ca, Hori found, increases all three refractive indices in the clinopyroxenes by 0·003 to 0·005; it is possible that the effect is about the same in the anthophyllites, but the data are as yet inadequate to draw definite conclusions, and the same applies to most of the other possible replacements.

*The use of weighting factors.*

It may occasionally happen that there are a few sets of observations of superior or inferior accuracy, and it is desirable to weight such data appropriately. This is readily done by the use of a weighting factor, but in choosing this factor it should be remembered that, for example, physical data of special accuracy do not merit special weight unless the accompanying chemical analyses are of comparable quality to the rest of the analyses.

If it is decided to use a weighting factor for certain sets of data, those sets should be multiplied by their appropriate weighting factors, which may be fractional for inferior data, before adding them to derive the weighted means, which will be given by relations of the type $\bar{x} = \sum W_i x_i / \sum W_i$. The data are now tabulated in the form of differences from the weighted means, and a column of weighting factors is added; the squares and products are formed as usual, except that each square or product is multiplied by the appropriate weighting factor

[1] F. Hori, Sci. Papers Coll. General Education Univ. Tokyo, 1954, vol. 4, no. 1, p. 71.

TABLE III. The formation of the matrix equation for the regression coefficients when a weighting factor is applied to part of the data; exemplified by the data for the *b* cell-dimension of anthophyllite. Compare tables I and IIB.

| No. | Si. | Mg. | Ca+Na+K. | *b*. | *W*. | *W*Si. | *W*Mg. | *W*(Ca+Na+K). | *Wb*. | $S^*\times10^2$. | $M^*\times10^2$. | $C^*\times10^2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6·20 | 3·37 | 0·41 | 17·96 | 2 | 12·40 | 6·74 | 0·82 | 35·92 | −88 | −97 | 22 |
| 8 | 6·50 | 3·78 | 0·08 | 17·86 | 2 | 13·00 | 7·56 | 0·16 | 35·72 | −58 | −56 | −11 |
| 9 | 6·60 | 3·93 | 0·12 | 17·84 | 2 | 13·20 | 7·86 | 0·24 | 35·68 | −68 | −41 | −7 |
| 14 | 6·82 | 4·34 | 0·02 | 17·70 | 2 | 13·64 | 8·68 | 0·04 | 35·40 | −26 | 0 | −17 |
| 17 | 7·01 | 3·67 | 0·29 | 17·99 | 2 | 14·02 | 7·34 | 0·58 | 35·98 | −7 | −67 | 12 |
| 20 | 7·42 | 2·67 | 0·00 | 18·14 | 1 | 7·42 | 2·67 | 0·00 | 18·14 | 34 | −67 | −19 |
| 26 | 7·83 | 4·83 | 0·08 | 18·08 | 1 | 7·83 | 4·83 | 0·08 | 18·08 | 75 | 49 | −11 |
| 29 | 7·85 | 5·95 | 0·37 | 17·94 | 2 | 15·70 | 11·90 | 0·74 | 35·88 | 77 | 61 | 18 |
| 30 | 7·84 | 5·51 | 0·16 | 18·02 | 2 | 15·68 | 11·02 | 0·32 | 36·04 | 76 | 17 | −3 |
| 43 | 7·76 | 6·04 | 0·31 | 17·94 | ½ | 3·88 | 3·02 | 0·15 | 8·97 | 68 | 70 | 12 |
| Sums | — | — | — | — | 16·5 | 116·77 | 71·62 | 3·13 | 295·81 | — | — | — |

| No. | $X^*\times10^2$. | $WS^2\times10^4$. | $WSM\times10^4$. | $WSC\times10^4$. | $WM^2\times10^4$. | $WMC\times10^4$. | $WC^2\times10^4$. | $WX^2\times10^4$. | $WSX\times10^4$. | $WMX\times10^4$. | $WCX\times10^4$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 15488 | 17072 | −3872 | 18818 | −4268 | 968 | 18 | −528 | −582 | 132 |
| 8 | −7 | 6728 | 6496 | 1276 | 6272 | 1232 | 242 | 98 | 812 | 784 | 154 |
| 9 | −9 | 9248 | 5576 | 952 | 3362 | 574 | 98 | 162 | 1224 | 738 | 126 |
| 14 | −23 | 1352 | 0 | 884 | 0 | 0 | 578 | 1058 | 1196 | 0 | 782 |
| 17 | 6 | 98 | 938 | −168 | 8978 | −1608 | 288 | 72 | −84 | −804 | 144 |
| 20 | 21 | 1156 | −5678 | −646 | 27889 | 3173 | 361 | 441 | 714 | −3507 | −399 |
| 26 | 15 | 5625 | 3675 | −825 | 2401 | −539 | 121 | 225 | 1125 | 735 | −165 |
| 29 | 1 | 11858 | 24794 | 2772 | 51842 | 5796 | 648 | 2 | 154 | 322 | 36 |
| 30 | 9 | 11552 | 17784 | −456 | 27378 | −702 | 18 | 162 | 1368 | 2106 | −54 |
| 43 | 1 | 2312 | 5780 | 408 | 14450 | 1020 | 72 | 1 | 34 | 85 | 6 |
| Sums | — | 65417 | 76437 | 325 | 161390 | 4678 | 3394 | 2239 | 6015 | −123 | 762 |

$$\begin{Vmatrix} 6{\cdot}5417 & 7{\cdot}6437 & 0{\cdot}0325 \\ 7{\cdot}6437 & 16{\cdot}1390 & 3{\cdot}4678 \\ 0{\cdot}0325 & 3{\cdot}4678 & 0{\cdot}3394 \end{Vmatrix} \bullet \begin{Vmatrix} s_x \\ m_x \\ c_x \end{Vmatrix} = \begin{Vmatrix} 0{\cdot}6015 \\ -0{\cdot}0123 \\ 0{\cdot}0762 \end{Vmatrix}.$$

* Composition and *b* parameters as differences from the weighted means. Weighted means:

$\overline{\text{Si}} = 116{\cdot}77/16{\cdot}5 = 7{\cdot}08$, $\overline{\text{Mg}} = 71{\cdot}62/16{\cdot}5 = 4{\cdot}34$, $\overline{\text{Ca+Na+K}} = 3{\cdot}13/16{\cdot}5 = 0{\cdot}19$, $\bar{b} = 295{\cdot}81/16{\cdot}5 = 17{\cdot}93$.

before summation (table III), and the matrix equation is set up, the covariance matrix calculated, and the calculation of the coefficients completed as above. There is, however, one further complication; in the calculation of the standard deviations of the dependent variables we have $\hat{\sigma}_x^2 \sum W_i = \sum W_i X_i^2 - a_x \sum W_i X_i A_i - b_x \sum W_i X_i B_i - \ldots$ instead of $N\hat{\sigma}_x^2 = \sum X_i^2 - a_x \sum X_i A_i - \ldots$. The formula for the standard deviations of the regression coefficients is not affected, and the number of degrees of freedom remains $N-n-1$.

*The evaluation of the covariance matrix; a systematic procedure.*

In the above discussion, the solution to the equation for the covariance matrix was shortly stated (p. 78) in the form: $\xi_{ij} = D_{ij}/D_0$, where $\xi_{ij}$ is the element in the $i$th row and $j$th column of the covariance matrix, $D_0$ is the determinant of the matrix of sums of squares and products of the independent variables, and $D_{ij}$ is the determinant derived by replacing the $i$th column of $D_0$ by the $j$th column of a unitary square matrix of order $n$, the number of independent variables. If $n = 2$ or 3, the formation and evaluation of these determinants presents no particular difficulties, but if there are many independent variables this process may become very tedious, and there are many opportunities for errors unless some systematic procedure is adopted. The procedure outlined below, based on successive pivotal reduction, has been found very effective in practice and includes adequate checks against arithmetical errors. It should be added that, since every step in the reduction of the determinants involves a subtraction of two numbers of the same order of magnitude, care must be taken to employ enough significant figures at each stage to ensure adequate accuracy in the final coefficients. With 2 or 3 significant figures in the observational data when expressed as differences from the means, 5 or 6 significant figures in the earlier stages of the reductions, and 4 or 5 in the last stages will not come amiss.

In the method of successive pivotal reduction for the evaluation of the determinants a determinant of order $q$ is reduced to one of order $q-1$ by the following relation, which is then applied again to reduce the order to $q-2$, and so on:

$$\begin{vmatrix} a_1 & b_1 & c_1 & \ldots & q_1 \\ a_2 & b_2 & c_2 & \ldots & q_2 \\ a_3 & b_3 & c_3 & \ldots & q_3 \\ . & . & . & \ldots & . \\ . & . & . & \ldots & . \\ a_q & b_q & c_q & \ldots & q_q \end{vmatrix} = \begin{vmatrix} B_2 & C_2 & \ldots & Q_2 \\ B_3 & C_3 & \ldots & Q_3 \\ . & . & \ldots & . \\ . & . & \ldots & . \\ B_q & C_q & \ldots & Q_q \end{vmatrix} \times \frac{1}{a_1^{q-2}},$$

where $B_2 = a_1b_2 - a_2b_1$, $E_4 = a_1e_4 - a_4e_1$, and similarly throughout. This method has the great advantage that the quantities $B_2$, $C_2$, &c., of the 'denominator determinant' $D_0$ recur in all the derived determinants $D_{ij}$ except the group $D_{1j}$. For if we replace the third column $c_1$, $c_2$,... of the left-hand determinant above by a new column $s_1$, $s_2$,..., then the determinant on the right will remain unchanged except for its second column $C_2$, $C_3$,..., which will be replaced by a new column $S_2$, $S_3$, where $S_2 = a_1s_2 - a_2s_1$, &c.; and if the $k$th column of the left-hand determinant is replaced by $s_1$, $s_2$,..., the $(k-1)$th column of the right-hand determinant will be replaced by $S_2$, $S_3$,.... The same, of course, applies to subsequent steps in the reductions. On this basis a systematic procedure for the reduction of the equation

for the covariance matrix is possible, in which $D_0$ and a proportion of the covariances are evaluated twice, so affording a check on the working.

Taking the covariance matrix for the refractive index data for anthophyllite as an example, we have:

$$\begin{Vmatrix} 4{\cdot}1476 & -0{\cdot}4356 & -1{\cdot}5162 & 4{\cdot}8148 & -0{\cdot}2226 \\ -0{\cdot}4356 & 0{\cdot}1265 & 0{\cdot}3478 & -0{\cdot}8315 & -0{\cdot}0175 \\ -1{\cdot}5162 & & 2{\cdot}0858 & -3{\cdot}6770 & -0{\cdot}0314 \\ 4{\cdot}8148 & & & 8{\cdot}2080 & -0{\cdot}1436 \\ -0{\cdot}2226 & & & & 0{\cdot}1888 \end{Vmatrix} \cdot \begin{Vmatrix} \xi_{ss} & \xi_{st} & \xi_{sf} & \xi_{sm} & \xi_{sc} \\ \xi_{ts} & \xi_{tt} & \xi_{tf} & \xi_{tm} & \xi_{tc} \\ \xi_{fs} & \xi_{ft} & \xi_{ff} & \xi_{fm} & \xi_{fc} \\ \xi_{ms} & \xi_{mt} & \xi_{mf} & \xi_{mm} & \xi_{mc} \\ \xi_{cs} & \xi_{ct} & \xi_{cf} & \xi_{cm} & \xi_{cc} \end{Vmatrix} = \begin{Vmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{Vmatrix}.$$

The first pivotal reduction of $D_0$, the determinant of the left-hand matrix (the matrix of sums of squares and products of the independent variables), gives:

$$D_0 = \begin{vmatrix} 4{\cdot}1476\times 0{\cdot}1265 - (0{\cdot}4356)^2 & 4{\cdot}1476\times 0{\cdot}3478 - 0{\cdot}4356\times 1{\cdot}5162 & -4{\cdot}1476\times 0{\cdot}8315 + 0{\cdot}4356\times 4{\cdot}8148 & -4{\cdot}1476\times 0{\cdot}0175 - 0{\cdot}4356\times 0{\cdot}2226 \\ & 4{\cdot}1476\times 2{\cdot}0858 - (1{\cdot}5162)^2 & -4{\cdot}1476\times 3{\cdot}6770 + 1{\cdot}5162\times 4{\cdot}8148 & -4{\cdot}1476\times 0{\cdot}0314 - 1{\cdot}5162\times 0{\cdot}2226 \\ & & 4{\cdot}1476\times 8{\cdot}2080 - (4{\cdot}8148)^2 & -4{\cdot}1476\times 0{\cdot}1436 + 4{\cdot}8148\times 0{\cdot}2226 \\ & & & 4{\cdot}1476\times 0{\cdot}1888 - (0{\cdot}2226)^2 \end{vmatrix} \times (4{\cdot}1476)^{-3}.$$

To find $D_{ij}$, we replace the $i$th column of the unreduced form of $D_0$ by the $j$th column of the right-hand unitary matrix; except when $i = 1$, the determinant so obtained will, after its first pivotal reduction, be identical with the first pivotal reduction of $D_0$, except in its $(i-1)$th column, which will be derived from the first column of $D_0$ and the $j$th column of the unitary matrix by the usual relation $B_2 = a_1b_2 - a_2b_1$.

We may therefore write the results of the first pivotal reduction thus:

$$D_0 = \begin{vmatrix} 0{\cdot}33492 & 0{\cdot}78208 & -1{\cdot}35140 & -0{\cdot}16955 \\ 0{\cdot}78208 & 6{\cdot}35220 & -7{\cdot}95052 & -0{\cdot}46774 \\ -1{\cdot}35140 & & 10{\cdot}86120 & 0{\cdot}47618 \\ -0{\cdot}16955 & & & 0{\cdot}73352 \end{vmatrix} \times (4{\cdot}1476)^{-3};$$

$$D_{(i+1),j} \propto \begin{Vmatrix} 0{\cdot}4356 & 4{\cdot}1476 & 0 & 0 & 0 \\ 1{\cdot}5162 & 0 & 4{\cdot}1476 & 0 & 0 \\ -4{\cdot}8148 & 0 & 0 & 4{\cdot}1476 & 0 \\ 0{\cdot}2226 & 0 & 0 & 0 & 4{\cdot}1476 \end{Vmatrix}$$

where the expression on the right is taken to indicate that $D_{(i+1),j}$ is derived by replacing the $i$th column of the left-hand expression for $D_0$ by the $j$th column of the right-hand matrix, each column of which is derived from the first column of $D_0$ and a column of the unitary matrix. Since $i$ is necessarily between 1 and 5 inclusive and the left-hand expression for $D_0$ has only four columns, $i+1$ must lie between 2 and 5 inclusive, so that the expression on the right cannot define $D_{ij}$ when $i = 1$.

We make further pivotal reductions in exactly the same manner, with the right-hand expression for $D_{(i+1),j}$ taking the place of the unitary matrix and combining with the first column of the reduced expression for $D_0$ to give the new expression for $D_{(i+2),j}$:

$$D_0 = \begin{vmatrix} 1{\cdot}51586 & -1{\cdot}60592 & -0{\cdot}02406 \\ -1{\cdot}60592 & 1{\cdot}81139 & -0{\cdot}06964 \\ -0{\cdot}02406 & & 0{\cdot}21693 \end{vmatrix} \times (4{\cdot}1476)^{-3} \times (0{\cdot}33492)^{-2};$$

$$D_{(i+2),j} \propto \begin{Vmatrix} 0{\cdot}16714 & -3{\cdot}24375 & 1{\cdot}38913 & 0 & 0 \\ -1{\cdot}02392 & 5{\cdot}60508 & 0 & 1{\cdot}38913 & 0 \\ 0{\cdot}14841 & 0{\cdot}70322 & 0 & 0 & 1{\cdot}38913 \end{Vmatrix}$$

$$D_0 = \begin{vmatrix} 0{\cdot}16684 & -0{\cdot}14420 \\ -0{\cdot}14420 & 0{\cdot}32826 \end{vmatrix} \times (4{\cdot}1476)^{-3} \times (0{\cdot}33492)^{-2} \times (1{\cdot}51586)^{-1};$$

$$D_{(i+3),j} \propto \begin{Vmatrix} -1{\cdot}28371 & 3{\cdot}28732 & 2{\cdot}33083 & 2{\cdot}10573 & 0 \\ 0{\cdot}22899 & 0{\cdot}98793 & 0{\cdot}03342 & 0 & 2{\cdot}10573 \end{Vmatrix}.$$

Finally, we evaluate

$$D_0 = 0{\cdot}033970/(4{\cdot}1476) \times (0{\cdot}33492)^2 \times 1{\cdot}51586 \doteq 2{\cdot}8000 \times 10^{-3},$$

while $D_{4j}$ and $D_{5j}$ ($j = 1, 2, 3, 4, 5$) are obtained by replacing the first and second columns respectively of the second-order determinant by the columns of the associated matrix of order $2 \times 5$.

$$\times 10^{-2}$$

$$D_{(i+3),j} = \begin{matrix} i+3 \\ 4 \\ 5 \end{matrix} \begin{Vmatrix} -3{\cdot}8837 & 12{\cdot}2155 & 7{\cdot}3711 & 6{\cdot}9122 & 3{\cdot}0365 \\ -1{\cdot}4691 & 6{\cdot}3886 & 3{\cdot}2727 & 3{\cdot}0365 & 3{\cdot}5131 \end{Vmatrix}$$

$$\begin{matrix} 1 & 2 & 3 & 4 & 5 \end{matrix} \quad = j.$$

And as $\xi_{ij} = D_{ij}/D_0$, we have:

$$\xi_{ij} = \begin{matrix} i= \\ 4 \\ 5 \end{matrix} \begin{Vmatrix} -11{\cdot}434 & 35{\cdot}962 & 21{\cdot}699 & 20{\cdot}348 & 8{\cdot}939 \\ -4{\cdot}325 & 18{\cdot}808 & 9{\cdot}634 & 8{\cdot}939 & 10{\cdot}342 \end{Vmatrix}$$

$$\begin{matrix} 1 & 2 & 3 & 4 & 5 \end{matrix} \quad = j.$$

So far, we have only derived the last two rows of the covariance matrix. By inverting the initial matrix of sums of squares and products of the independent variables, bringing 0·1888 to the top left corner and 4·1476 to the bottom right, and reducing in the same way, we can derive two more rows (the first two). To derive the third row we must return to that stage of reduction at which $D_0$ is expressed as a third order determinant. If we replace the first column of this determinant by each of the five columns of the associated matrix of order $3 \times 5$, the five resulting third-order determinants will be the five $D_{3j}$; and since $5-2 = 1+2 = 3$, the same five determinants will result by treating the third-order stage of the reduction of the inverted matrix of sums of squares and products in the same way:

$$D_{31} = \begin{vmatrix} 0{\cdot}16714 & -1{\cdot}60592 & -0{\cdot}02406 \\ -1{\cdot}02392 & 1{\cdot}81139 & -0{\cdot}06964 \\ 0{\cdot}14841 & -0{\cdot}06964 & 0{\cdot}21693 \end{vmatrix} \times P^{-1}; \quad D_{32} = \begin{vmatrix} -3{\cdot}24375 & -1{\cdot}60592 & -0{\cdot}02406 \\ 5{\cdot}60508 & 1{\cdot}81139 & -0{\cdot}06964 \\ 0{\cdot}70322 & -0{\cdot}06964 & 0{\cdot}21693 \end{vmatrix} \times P^{-1};$$

$$D_{33} = 1{\cdot}38913 \times \begin{vmatrix} 1{\cdot}81139 & -0{\cdot}06964 \\ -0{\cdot}06964 & 0{\cdot}21693 \end{vmatrix} \times P^{-1}; \quad D_{34} = 1{\cdot}38913 \times \begin{vmatrix} 1{\cdot}60592 & 0{\cdot}02406 \\ -0{\cdot}06964 & 0{\cdot}21693 \end{vmatrix} \times P^{-1};$$

$$D_{35} = 1{\cdot}38913 \times \begin{vmatrix} 1{\cdot}60592 & 0{\cdot}02406 \\ -1{\cdot}81139 & 0{\cdot}06964 \end{vmatrix} \times P^{-1}; \text{ where } P = (4{\cdot}1476)^3 \times (0{\cdot}33492)^2.$$

These five determinants are then evaluated and divided by $D_0$ to give the five elements $\xi_{3j}$.

If our example had more independent variables, it would be necessary to go farther back to complete the covariance matrix: with seven variables, the first step, with direct and inverted matrices, would give rows 1, 2, 6, and 7; rows 3 and 5 could be derived from the third-order determinants, but row 4 must be derived from the fourth-order stage in the reduction of $D_0$ and its associated matrix.

In this procedure, every element of the covariance matrix is determined twice, except those in the principal diagonal, so affording an almost complete check. If the number of independent variables is high, it may be felt that so complete a check is superfluous, and it is quite a simple matter to omit some of the check calculations. Thus in our fifth-order example, after the first two and last two rows have been calculated, we may utilize the symmetry relation $\xi_{ij} = \xi_{ji}$ to write in the first two and last two columns, leaving only $\xi_{33}$ to be determined.

# *Re-examination of the mineral tuhualite*

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[Taken as read 3 November 1955.]

*Summary.*—X-ray study of tuhualite from Mayor Island, New Zealand, has shown it to be orthorhombic, space-group either $Cmca = D_{2h}^{18}$ or $C2ca = C_{2v}^{17}$. Unit-cell dimensions are $a = 14{\cdot}31$ Å., $b = 17{\cdot}28$ Å., $c = 10{\cdot}11$ Å., and $a : b : c = 0{\cdot}828 : 1 : 0{\cdot}585$. Goniometric measurements give $a : b : c = 0{\cdot}8243 : 1 : 0{\cdot}5658$. $a\{100\}$ dominant with forms $s\{011\}$, $p\{021\}$, $c\{001\}$, $b\{010\}$, $n\{101\}$, $m\{110\}$, $q\{111\}$. Crystals with $b\{010\}$ dominant are rare. Three good cleavages, $a$ (100), $b$ (010), $c$ (001). $\alpha = 1{\cdot}608$, $\beta = 1{\cdot}612$, $\gamma = 1{\cdot}621$; $\gamma - \alpha = 0{\cdot}013$. $2V = 61_D^\circ$–$70_v^\circ$, positive; $\beta = b$, $\gamma = c$, $\alpha =$ colourless to pale lavender, $\beta =$ violet, lavender, $\gamma =$ intense purplish-blue; $\gamma > \beta > \alpha$. Sp. gr. 2·89 (measured), 2·86 (calculated).

An analysis of carefully purified material leads to the possible formula:

$$H_9(Na,K,Mn)_{12}Fe_6''(Al,Fe''',Mg,Ti)_9[Si_3O_8]_{15}.$$

Details of alteration phenomena and associated minerals are given. Occurrence is held to result by crystallization from magma quite impoverished in lime due to early fractionation of aegirine-hedenbergite, and perhaps aegirine-augite, in the intratelluric stage.

TUHUALITE is a constituent of ejectamenta on Mayor Island, New Zealand, at and in the vicinity of Opo Bay at the southern extremity of the island, and occurs *in situ* in banded rhyolites that outcrop along the base of the caldera wall just north-east of Tutaretare (1162 feet). Mayor Island, the Maori name for which is Tuhua, lies in latitude 37° 20′ South and longitude 176° 15′ East, within the Bay of Plenty off the east coast of North Island, New Zealand. The island is a volcanic cone with an elevation of 1274 feet above sea-level. The rocks are acidic in character and consist of a series of lavas, often pure obsidians, and tuffs, and most if not all of these have comenditic affinities.

The first record of the paragenesis and properties of tuhualite is found in a preliminary account of some volcanic rocks from North Island, New Zealand, by Marshall (1932, p. 202). In that paper attention was called to the presence in comendites on Mayor Island of 'a supposedly new amphibole with the extraordinary pleochroism, colorless to purplish violet to deep violet', in association with the sodic ferromagnesian constituents aegirine, cossyrite, and arfvedsonite; the last mineral was subsequently shown to be riebeckite (Marshall, 1936A, p. 341).

Later, Marshall (1936B) published a more detailed paper on tuhualite. Crystallographic measurements that were secured with the aid of a stage

goniometer are reported and these data led to the belief that the mineral was orthorhombic with $a:b:c = 0{\cdot}915:1:0{\cdot}512$. On the basis of these data Marshall came to the conclusion that his previous opinion that the mineral was an amphibole was an incorrect one. Some optical data, determined by other workers, are reported, and finally Marshall listed four analyses of comendites made by Mr. F. T. Seelye, one supposedly devoid of tuhualite, which in the present writer's opinion do not differ in any significant degree from one another. However, on the basis of the supposed differences between these analyses Marshall calculated a composition for tuhualite itself (table III, anal. B).

The petrography of the Mayor Island sodic rhyolites had been investigated previously; von Wolff (1904) described material donated by Thilenius, and J. A. Bartrum (1926) carefully studied specimens collected by J. A. Thomson during the latter's visit to the island in 1920, and also some thin sections lent to him by Speight. Marshall visited the island on at least two occasions and collected the material that formed the basis of three papers (Marshall, 1932, 1936A, 1936B).

The new analysis and the crystallographic and X-ray studies of tuhualite reported on herein were made with material obtained from specimens collected by Marshall himself, and some incidental observations on mineral association were made with material collected by others. A few crystal measurements were also performed on material given to the writer by Dr. P. G. Harris, who had in the first place obtained it from Marshall.

*Occurrence of tuhualite.*

In the material examined by this writer tuhualite has been found to occur as follows: (*a*) As a constituent of crudely microspherulitic aggregates of felspar, quartz, aenigmatite, riebeckite, and acgirine in the groundmass of both non-porphyritic and coarsely porphyritic comendites; and there appears to be every gradation between this association and microstructure and that in which tuhualite in irregular, moss-like outline, almost pigmentary in form, is intimately associated with alkali-felspar, quartz, and any one or combination of the sodic ferromagnesian constituents on a microcrystalline scale with or without marked flow structures. In a number of instances tuhualite is sufficiently abundant to produce deep blue areas that are quite obvious megascopically. However, it should be pointed out that the percentage of tuhualite in these areas is low and in no case has the present writer found it to make up 50 % of such areas (cf. Marshall, 1936B, p. 335). (*b*) More

or less equidimensional subeuhedral isolated crystals up to 0·25 mm. in diameter, which are often situated in portions of the rock somewhat more coarsely crystalline than the average. (*c*) As euhedra (1·5 mm. in length) in very porous, pale grey zones in comendite, and in steam cavities where the best euhedra have been noted; these may occur alone or with either stout euhedra of aegirine or flat prismatic crystals of riebeckite, or both.

In many of the rhyolites examined, most of which were devoid of tuhualite, a pale greenish-yellow to orange-yellow mineral of serpentinous appearance was recognized; it is especially well developed in the dark-coloured, finely banded rocks from the crater area and gives rise to the narrow yellow bands therein as seen in hand specimens. For it the following properties have been determined: $\gamma-\alpha < 0{\cdot}010$; $n = 1{\cdot}547$–$1{\cdot}551$; pleochroism not recognizable.

A second, but uncommon, yellow mineral of irregular outline occurs in the tuhualite-bearing comendites, and this may be the material commented upon by Marshall (1936B, p. 336), although it is quite uncertain whether Marshall was referring to this or to the more abundantly developed yellow serpentinous material just mentioned. It has the following optical properties: $\alpha = 1{\cdot}603 \pm 0{\cdot}003$, $\beta = 1{\cdot}613$, $\gamma = 1{\cdot}620$, $\gamma-\alpha = 0{\cdot}017$. Optic axial angle measurements gave: 82° (−), 66° (−); for a strongly zoned crystal: inner zone = 64° (−), outer zone = 72° (−). Dispersion is strong in most fragments with $\rho < v$, although this is absent in a few instances. Pleochroism is faint, with $\alpha$ = pale yellowish-green, $\gamma$ = pale yellow; $\gamma \geqslant \alpha$. At least one good cleavage is evident with extinction oblique thereto. In the yellow mineral noted by Marshall lamellar twinning appeared to be common; this property was not observed in any of the examples studied at this time.

The similarity of the refractive indices of this mineral to those of tuhualite is interesting, especially so since instances have been found occasionally where crystals exhibit gradations from tuhualite-like material outwards into the clear yellow mineral of unknown composition.[1]

### *Physical properties.*

Tuhualite is excessively brittle, so much so that any attempt to release a crystal from attachment to a vesicle wall causes severe fracturing of the crystal. Accordingly the fragments used for X-ray and other work

[1] A very faint X-ray diffraction pattern obtained from a minute amount of this mineral exhibited two lines at $d = 3{\cdot}45$ Å. and 3·35 Å. in order of decreasing intensity.

never exceeded 0·25 mm. Three good pinacoidal cleavages are present, but that perpendicular to the vertical crystallographic axis, the acute bisectrix, appears to be superior to the other two.

It was found that most of the crystal fragments were contaminated by adhering quartz or felspar, or both, and therefore specific gravity determinations were made by repeatedly centrifuging the pure mineral powder obtained for analysis in methylene iodide-bromoform-acetone mixtures; a value of $2{\cdot}89 \pm 0{\cdot}02$, corrected for determination made at 20° C., was obtained, and this corresponds closely with values secured from seven fragments whose purity could not be absolutely guaranteed, $2{\cdot}88 \pm 0{\cdot}02$. Hardness, determined with a fine needle point on the surfaces of a crystal cemented to a glass slide, is about 3 to 4.

Refractive indices and pleochroism for tuhualite as analysed were found to be: $\alpha = 1{\cdot}608 \pm 0{\cdot}001$, $\beta = 1{\cdot}612$, $\gamma = 1{\cdot}621 \pm 0{\cdot}003$, $\gamma - \alpha = 0{\cdot}013$; $\alpha$ = colourless to very pale pink, $\beta$ = violet or lavender, $\gamma$ = intense purplish-blue; $\gamma > \beta > \alpha$, with much less difference between $\beta$ and $\gamma$ than between $\beta$ and $\alpha$.

The limits of error are much wider in the case of the $\gamma$-vibration direction of the refractive index ellipsoid owing to intense absorption, even in fragments less than 20 microns in thickness. Refractive indices for the $\alpha$-vibration direction in a number of crystal fragments not included in the analysed material were: 1·604, 1·609, and 1·606. These values possibly indicate a range of chemical composition from grain to grain, and zoning was clearly observed during measurement of 2V, although colour and pleochroism did not seem to be correspondingly affected.

The values obtained for the analysed material reported on in this paper differ appreciably from those determined for a crystal of tuhualite by the present writer in 1935 at the request of Marshall. The reason for this discrepancy is not clear at this stage.

The mineral is optically positive, and optic axial-angle measurements made in monochromatic light of wavelengths 4900 Å. and 6026 Å. (values for the latter in parentheses) gave a distinct range of values as follows: analysed material 70° (61°–62°), crushed crystal fragments 76°, 78°, 76° (70°, 72°, 69°); a zoned crystal gave 76° (68°) for centre, 80° (70°) for median zone, and 91° (82°) for a narrow peripheral zone. Dispersion of the optic axes is strong with $\rho < v$, and the optic axial plane is parallel to (010), that is, $\beta = b$. Elongation positive, $\gamma = c$.

As distinct from gradation of tuhualite into the yellow mineral of undetermined composition, clearly a magmatic reaction, tuhualite has undergone changes due to weathering. There is no doubt that the end-

products are red-brown patches of limonitic iron oxides, but intermediate stages are less clear. Early in the breakdown, however, a slight loss of colour with almost complete loss of pleochroism and diminution in birefringence takes place, and in the few instances observed such crystals were optically negative (change of sign) with 2V close to 30°. A later

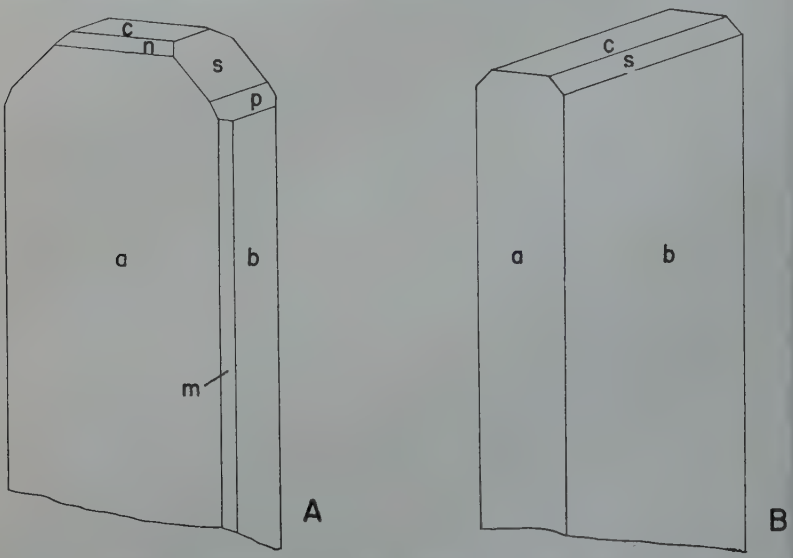


Fig. 1. Crystals of tuhualite from Mayor Island. A, common habit; B, rare habit.

stage involves development of isotropy and appearance of iron stain, although moderate absorption in lavender remains. Rare crystal fragments, colourless but otherwise comparable to tuhualite, have been recognized; to what stage in the decomposition process such fragments belong, if they do, is unknown.

When the Gladstone and Dale formula $(n-1)/D = K$ is applied to tuhualite the value of $K$, 0·2154, derived from the physical constants, approximates fairly closely to that obtained from the composition (0·2183); these values are comparable to those found for close-packed structures.

*Morphology.*

Examination of crystals that were carefully removed from steam cavities shows that the form $a\{100\}$ is usually dominant with $s\{011\}$, $p\{021\}$, $c\{001\}$, and $b\{010\}$ about equally developed (fig. 1A). $m\{110\}$ and $n\{101\}$ are slightly less well developed in the crystal figured (fig. 1A);

on the other hand, a few stumpy crystals were found to exhibit about equal development of the forms $a\{100\}$, $b\{010\}$, $m\{110\}$, with $c\{001\}$, $n\{101\}$, and $s\{011\}$ as the only terminal forms. Rarely crystals were noted with $b\{010\}$ dominant, $a\{100\}$, $c\{001\}$, and $s\{011\}$ as sole forms (fig. 1B). $q\{111\}$ appears to be uncommon.

No crystals were found suitable for accurate goniometric treatment owing to small size and to curvature or irregularity of faces. However, approximate measurements were made, in some instances with the Fedorov stage and stage micrometer, and these data are compared with Marshall's values and the angles calculated from the structural cell in table I. Since the X-ray data were secured from a greater number of measurements more weight should be attached to the values in column C of table I.

TABLE I. Angle table for tuhualite: A, based on goniometric measurements (zone adjusted, [001]; $b$ (010) at $\phi = 0°$) compared with B, angles based on the measurements of Marshall (1936B), and C, angles calculated from the X-ray data. Marshall also cites $aq$ 52·0° (calc. 58° 39′).

| | A. | | B. | | C. | |
|---|---|---|---|---|---|---|
| | $\phi$. | $\rho$. | $\phi$. | $\rho$. | $\phi$. | $\rho$. |
| $n$ (101) | 90° 00′ | 34° 30′ | — | — | 90° 00′ | 35° 15′ |
| $s$ (011) | 0° 00′ | 29° 30′ | 0° 00′ | 27° 24′ | 0° 00′ | 30° 22′ |
| $p$ (021) | 0° 00′ | 48° 00′ | 0° 00′ | 50° 24′ | 0° 00′ | 49° 29′ |
| $m$ (110) | 50° 30′ | 90° 00′ | 47° 42′ | 90° 00′ | 50° 18′ | 90° 00′ |
| $q$ (111) | 50° 30′ | 42° 00′ | — | — | 50° 18′ | 42° 33′ |

*X-ray study.*

A camera of diameter 114·59 mm. and manganese-filtered iron-radiation, Fe-$K_\alpha$ = 1·9373 Å., were used to obtain powder photographs of tuhualite as analysed. Many of the reflections, however, are weak and diffuse, particularly in the region of high $2\theta$ values, and therefore it was not possible to measure the latter with acceptable accuracy. The X-ray powder data are set out in table II together with indices and spacings that have been calculated from the lattice dimensions secured from rotation and Weissenberg photographs, obtained with the crystal fragment figured (fig. 1A): $a = 14{\cdot}31 \pm 0{\cdot}03$ Å., $b = 17{\cdot}28 \pm 0{\cdot}03$ Å., $c = 10{\cdot}11 \pm 0{\cdot}03$ Å. Cell volume = 2499·96 Å.$^3$, and with the sp. gr. a cell weight of $7224{\cdot}88 \times 10^{-24}$ g. is found.

This leads to an axial ratio of $a:b:c$ of 0·828:1:0·585. Calculation of the density from the relation $D = 1{\cdot}66030 \sum A/V$ and employing the formulary quantities in column D of table IV gave 2·86, a figure that is slightly less than that determined experimentally.

Systematic indexing of the Weissenberg patterns indicated that the space-group is either $Cmca = D_{2h}^{18}$ or $C2ca = C_{2v}^{17}$.

TABLE II. Powder pattern of tuhualite, Opo Bay, Mayor Island; Fe-$K_\alpha$ radiation with $\lambda$ 1·9373 Å. Camera diameter 114·59 mm. Intensities estimated visually.

| *hkl.* | *d* (obs.) | *d* (calc.) | *I.* | *hkl.* | *d* (obs.) | *d* (calc.) | *I.* |
|---|---|---|---|---|---|---|---|
| 020 | 8·62 | 8·62 | s | 004 | 2·522 | 2·528 | vw |
| 200 | 7·16 (A) | 7·16 | vs | 062 | | 2·52 | |
| 220 | 5·515 | 5·515 | s | 531 | 2·490 | 2·485 | m |
| 130 | 5·34 | 5·34 | vvw | 442 | 2·416 | 2·42 | w |
| 002 | 5·04 | 5·05 | w | 204 | 2·378 | 2·382 | vvw |
| 221 | 4·85 | 4·85 | s | 153 | | 2·379 | |
| 310 | 4·57 | 4·60 | vw | 171 | 2·362 | 2·366 | vw |
| 022 | 4·35 | 4·36 | s | 423 | | 2·36 | |
| 040 | 4·315 | 4·32 | s | 461 | 2·184 | 2·19 | s |
| 202 | 4·115 | 4·12 | vw | 353 | 2·147 | 2·153 | vw |
| 041 | 3·96 | 3·97 | w | — | 2·078 | — | vvw |
| 222 | 3·71 | 3·72 | s | — | 2·053 | — | vvw |
| 240 | | 3·70 | | — | 2·002 | — | w |
| 330 | 3·67 | 3·67 | m | — | 1·974 | — | w |
| 132 | | 3·67 | | — | 1·937 | — | vvw |
| 400 | 3·58 | 3·58 | m | — | 1·887 | — | vvw |
| 241 | 3·47 | 3·475 | s | — | 1·86 | — | vw |
| 331 | | 3·455 | | — | 1·839 | — | vw |
| 420 | 3·31 | 3·305 | m | — | 1·789 | — | w |
| 042 | 3·285 | 3·285 | m | — | 1·767 | — | vvw |
| 113 | 3·22 | 3·22 | m | — | 1·726 | — | s |
| 151 | 3·18 (C) | 3·19 | s | — | 1·669 | — | vvw |
| 421 | 3·14 | 3·145 | m | — | 1·653 | — | vvw |
| 242 | 2·97 | 2·984 | m | — | 1·550 | — | vw |
| 402 | 2·926 | 2·921 | w | — | 1·535 | — | vw |
| 060 | 2·87 | 2·88 | vw | — | 1·501 | — | vvw |
| 133 | | 2·851 | | — | 1·483 | — | vw |
| 061 | 2·766 (B) | 2·77 | s | — | 1·452 | — | w |
| 422 | | 2·766 | | | | | |
| 440 | 2·75 | 2·755 | vvw | | | | |
| 441 | 2·657 | 2·659 | m | | | | |
| 043 | | 2.658 | | | | | |

And numerous other lines at greater $2\theta$ values that could not be measured with desirable accuracy.

A, B, and C: Most prominent lines, decreasing in intensity in order A to C.

### *Chemical composition.*

A large sample of comendite, approximately 820 g. in weight, was broken down to $< 30$ micron particle size by crushing, screening, and elutriation. The total bulk of this material was then centrifuged in a bromoform-acetone mixture of density 2·70, and from the heavy fraction so obtained an apparently pure sample of tuhualite weighing 0·92 g. was secured by repeated centrifugal fractionation. As purification of the

sample proceeded, fine-grinding carefully performed under alcohol was required in order to free tuhualite particles from contaminating quartz, felspar, riebeckite, &c. The separation was carried out approximately quantitatively, and the small quantity recovered gives a good indication of the percentage of tuhualite in the rock in spite of the fact that the original sample exhibited many deep-blue patches. It will be recalled that Marshall (1936B, p. 335) expressed the opinion that the blue patches contained approximately 50 % of tuhualite.

Scarcity of material did not permit any chemical tests beyond those that indicated that tuhualite is not noticeably affected by either hot concentrated HCl or $H_2SO_4$ after five minutes of such treatment. Analyses of comendite and tuhualite are set out in table III, and analysis C of

TABLE III. Analyses of comendite and tuhualite from Opo Bay, Mayor Island, New Zealand.

| | A. | B. | C. |
|---|---|---|---|
| $SiO_2$ ... | 72·28 | 75·36 | 62·93 |
| $Al_2O_3$ ... | 9·75 | 9·33 | 0·63 |
| $Fe_2O_3$ ... | 4·44 | 3·61 | 14·09 |
| FeO ... | 1·43 | 2·33 | 9·58 |
| MgO ... | 0·28 | 0·06 | 0·42 |
| CaO ... | 0·44 | 0·25 | tr. ? |
| $Na_2O$ ... | 4·96 | 4·75 | 7·11 |
| $K_2O$ ... | 4·50 | 4·06 | 1·74 |
| $H_2O^-$ ... | 1·04 | 0·21(−) | 0·38 |
| $H_2O^+$ ... | 0·68 | 0·12(−) | 1·61 |
| $TiO_2$ ... | 0·23 | 0·23 | 0·42 |
| $P_2O_5$ ... | 0·04 | — | nil |
| MnO ... | 0·14 | 0·18 | 0·81 |
| | 100·44 | 100·16 | 99·72 |
| O for F ... | 0·03 | | |
| | 100·41 | | |

A. Comendite, Mayor Island. Anal. F. T. Seelye (Marshall, 1936A, p. 343). Also S 0·02, $ZrO_2$ 0·03, rare earths 0·10, Cl 0·02, F 0·06 %. $B_2O_3$, NiO, BaO, SrO, and $CO_2$ 0·00 %.

B. Marshall's analysis of tuhualite arrived at by calculation (Marshall, 1936B, p. 335). Negative values for water are neglected in summation.

C. Tuhualite, Mayor Island. Anal. C. Osborne Hutton.

this table has been recalculated to determine the number of atoms of each kind in the empirical unit-cell (table IV), with full consideration given to the probable errors incurred in the physical measurements and chemical analysis.

On the basis of the calculations summarized in table IV, the actual numbers of (O,OH) atoms in the unit-cell lie between 119·90 and 122·42,

TABLE IV. Empirical unit-cell contents of tuhualite with probable errors based on the assessed errors of the chemical analysis and the physical data.

| | | A. | | B. | C. | D. | E. |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | ... ... | 62·93±0·20 | Si | 45·89 | ±0·46 | 45·45 | 0·43 |
| $Al_2O_3$ | ... ... | 0·63±0·30 | Al | 0·53 | ±0·26 | 0·53 | 0·50 |
| $Fe_2O_3$ | ... ... | 14·09±0·40 | $Fe'''$ | 7·72 | ±0·23 | 7·65 | 0·60 |
| MgO | ... ... | 0·42±0·10 | Mg | 0·44 | ±0·11 | 0·45 | 0·65 |
| $TiO_2$ | ... ... | 0·42±0·04 | Ti | 0·22 | ±0·02 | 0·22 | 0·68 |
| FeO | ... ... | 9·58±0·30 | $Fe''$ | 5·83 | ±0·18 | 5·78 | 0·75 |
| MnO | ... ... | 0·81±0·02 | Mn | 0·49 | ±0·01 | 0·49 | 0·80 |
| $Na_2O$ | ... ... | 7·11±0·20 | Na | 10·04 | ±0·30 | 9·95 | 0·95 |
| $K_2O$ | ... ... | 1·74±0·06 | K | 1·61 | ±0·05 | 1·59 | 1·33 |
| $H_2O$ | ... ... | 1·61±0·25 | (OH) | 7·83 | ±1·22 | 7·75 | — |

$\delta a/a = 0{\cdot}00209$; $\delta b/b = 0{\cdot}00173$; $\delta c/c = 0{\cdot}00296$; $\delta D/D = 0{\cdot}00692$.
D (corrected) = 2·89±0·02.
Conversion factor $F = (abcD)/(1{\cdot}6603 \times 99{\cdot}34) = 43{\cdot}804$.
Cell volume = 2499·96 Å.$^3$
Cell weight = $7224{\cdot}88 \times 10^{-24}$ g.
% oxygen in tuhualite = $121{\cdot}16 \times 16/F = 44{\cdot}25$ %.
Error due to the FeO determination ($F\delta P/2m$) = 0·091.
Total error in Σ (O,OH) = 1·26.
Total error in O = 1·21.
Σ (Al,$Fe'''$,Mg,Ti) = 8·99±0·37.
Σ (Mn,Na,K) = 12·14±0·33.
Σ (O,OH) = 121·16±1·26.
Total iron as $Fe_2O_3$ = 24·74±0·25.

Possible formula of tuhualite: $H_9(Na,K,Mn)_{12}Fe''_6(Al,Fe''',Mg,Ti)_9[Si_3O_8]_{15}$.

A. Weight % of oxides (= $P$).
B. Empirical unit-cell contents, $FPm/M$ (Min. Mag., 1954, vol. 30, p. 481).
C. $\delta E$ = assessed probable errors due to $\delta_c E$ (derived from the chemical analysis) and $\delta_p E$ (derived from the physical data).
D. Number of atoms on the basis of 120 (O,OH) atoms to the unit-cell.
E. Ionic radii according to Pauling.

and accordingly 120 is suggested as a probable figure in this instance. Further, the integers 9, 6, and 12 are clearly within the limits of error for the $Fe'''$, $Fe''$, and Na groups. It might be pointed out that inclusion of Mg with the $Fe'''$ group rather than with $Fe''$ is more appropriate in view of the values of the ionic radii concerned. The amount by which Si departs from the integral value of 45 suggests possible quartz impurity in the analysed material, but if this is the answer, the weight % of quartz contaminant would not appear to exceed 0·6.

Accordingly it is suggested that the empirical unit-cell contents of tuhualite may be represented by the formula:

$$H_9(Na,K,Mn)_{12}Fe''_6(Al,Fe''',Mg,Ti)_9(Si_3O_8)_{15}.$$

*Petrogenesis.*

Comendites and pantellerites are well developed in widely scattered localities—Sardinia, Pantelleria, Queensland, New South Wales, and British East Africa, to mention a few—and they have been closely studied. But in none of these occurrences has tuhualite been observed in the acid lavas, and since its optical properties are so distinctive it is unlikely that it could have been overlooked. Accordingly, the unique occurrence of tuhualite in Mayor Island rocks is doubly interesting since the composition of these rocks (table III, analysis A) does not differ in any significant detail from many described from Sardinia, Pantelleria, and East Africa. One is therefore tempted to conclude that critical conditions of temperature and pressure rather than unique composition of magma might be the important factor in permitting crystallization of this mineral.

Study of numerous specimens shows that tuhualite has crystallized either in association with quartz and felspar in the groundmass, or at the latest stage, often accompanied by riebeckite and aegirine, in vesicles, and the present study has not shown it to be a member of the intratelluric mineral assemblage which includes quartz, sanidine, sodic pyroxene, and aenigmatite.

Incomplete study shows that the phenocrystic pyroxene is often strongly zoned, with wider extinction angles than those usually recognized for aegirine. For several phenocrysts the following properties were found:[1] $\alpha \wedge c = 25°$, $2V = 72°$ (+); $\alpha \wedge c = 23°$, $2V = 88°$ (+), $\rho < v$ strong; $\alpha \wedge c = 12°$, $\gamma = 1{\cdot}785$. A marked decrease in extinction angle was evident in some peripheral zones. These data suggest that much of the phenocrystic pyroxene is aegirine-hedenbergite rather than aegirine in composition, with perhaps diopside also entering into the composition. For crystals separated from vesicles much smaller extinction angles were generally represented, and the following data appeared to be typical: $\alpha = 1{\cdot}758, \gamma = 1{\cdot}810, \alpha \wedge c = 0$ to $2°$; dispersion not strong. Incomplete as these data are it would seem as if the vesicle crystals are closer to aegirine in composition than is the phenocrystic material.

Therefore it is suggested that early separation of hedenbergitic or diopsidic aegirine in the form of phenocrysts has more or less exhausted the originally small supply of lime, but not of alkalis and iron, in the magma; this has resulted, at a later stage, in crystallization of

[1] Fedorov stage determinations employing hemispheres of $n = 1{\cdot}649$; angles of tilt were corrected.

aegirine,[1] with presumably negligible calcium content, and tuhualite devoid of that element. Accordingly an appeal to special pressure-temperature conditions would seem to be unnecessary.

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[1] Rare earths were detected qualitatively in a very small sample of aegirine separated from vesicles in the comendites, a circumstance not uncommon in such pyroxenes (H. S. Washington and H. E. Merwin, Amer. Min., 1927, vol. 12, p. 236). Undoubtedly this accounts, in some measure at least, for the rare earths reported in the comendite analysis, but for which a location was not indicated by Marshall (1936a, p. 343).